Ionization Energies and Dyson Orbitals of Cytosine and 1-Methylcytosine

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Electron propagator methods are applied to the vertical ionization energies of the five most stable tautomers of cytosine and to two oxo forms of 1-methylcytosine. For both molecules, there are several isomers within a few kcal/mol of each other. Ionization energies for each isomer have been calculated, therefore. The lowest feature in gas phase photoelectron spectra corresponds to π_1 holes, but broad, higher-energy peaks are produced by two or three cationic states in each isomer. The order of final states is π_1, π_2, n_1, n_2, π_3, π_4 for all isomers except the amino−oxy forms of cytosine, where the order is π_1, n_1, π_2, n_2, π_3, π_4.

Introduction

Electronic structure in nucleobases and their cations influences phenomena as diverse as radiation damage of genetic material, electron transport in helical stacks, and the reactivity of radical species with nucleic acids. Various types of photoionization spectroscopy therefore have been applied to nucleic acid fragments.[1−4] Photoelectron spectra (PES) of all unsubstituted and some methylated nucleobases have been reported.[5−16] Very often, these spectra are hard to assign because of tautomerism. Of all of the nucleobases, cytosine and guanine may have the largest number of tautomers in the gas phase.[17,18]

PES of gas phase cytosine have been available for some time.[12,14,15] These spectra exhibit many wide, overlapping bands, some with complex vibrational structure, that have proven difficult to resolve. In these works, tentative assignments were proposed. The complicated structures of these spectra are likely to originate in the presence of more than one isomeric form of a given molecule in the gas phase.

Recently, it has been shown by high-level ab initio calculations that free cytosine might exist in a number of tautomeric forms that are very close in energy.[19,20] Six low-lying cytosine tautomers were found, and their relative stability depended upon basis set and correlation approximations. Three tautomers were shown to be within 0.8 kcal/mol of each other. A very recent work on the subject of tautomerism in cytosine revealed close energetic proximity between amino−oxo and imino−oxo forms.[21]

Substituted species often provide useful, contrasting PES. Methylation of cytosine in the N_1 position eliminates the possibility of oxo−oxy tautomerism; therefore, the spectrum of N_1-methylcytosine was recorded to aid assignments for cytosine and its derivatives.[14,16]

Here, we present the results of ab initio electron propagator calculations[22] in the P3[23,24] approximation for five tautomers of cytosine and amino− and imino−oxo forms of N_1-methylcytosine. Assignments of the spectra are made, and all isomeric structures are shown to contribute to the PES. Dyson orbital (DO) descriptions are provided for each photoionization final state.

Methods

All calculations were performed with GAUSSIAN-99.[25] Optimizations were performed with second order perturbation theory total energies and the 6-311G** basis set.[26] Nonplanarity in the amino groups was explicitly considered; no symmetry constraints were imposed. The five lowest tautomeric structures are in qualitative agreement with the results of ref 19, but the minima are nonplanar. A sixth tautomer lies 9.2 kcal/mol above the lowest isomer and is therefore unlikely to be pertinent to the photoelectron spectra.

Optimized geometries were used for propagator calculations with the same basis set. The P3 electron propagator approximation[23] and the 6-311G** basis set have been shown to give excellent agreement with experimental PES for all other nucleic acid bases[27−29] and a number of organic molecules.[30−33] Average errors of 0.1−0.2 eV are typical for this kind of calculation. All virtual and occupied valence molecular orbitals (MOs) were retained in the propagator calculations.

For every vertical ionization energy (IE) calculated with electron propagator theory, there corresponds a DO such that

$$\phi_i^{\mathrm{DO}}(x_1) = \int \Psi_{\mathrm{molecule}}(x_1, x_2, x_3, ..., x_N)\Psi^*_{\mathrm{cation},i}(x_2, x_3, x_4, ..., x_N)\, dx_2\, dx_3\, dx_4 ... dx_N \quad (1)$$

where the molecule has N electrons and the cation in state i has $N - 1$ electrons.[22] Integration over all electronic degrees of freedom except one (x_1) produces the DO, which describes the change in electronic structure that accompanies the removal of an electron. For each cationic state, i, there is a different DO, ϕ_i^{DO}.

Molecular structures and DO diagrams were graphed with the MOLDEN package.[34] Contours of ±0.03 for each DO are presented in the figures.

Results and Discussion

Relative energies of tautomers are given in Table 1. Molecular structures are depicted in Figures 1 and 2. Theoretical spectra are compared with PES in Tables 2−7. All pole strengths exceed 0.84; the perturbative propagator methods employed presently therefore are very likely to be valid. Corresponding DOs are displayed in Figures 3−6. The following notations are used throughout the paper for tautomeric structures: Cy0, 1H-amino−oxo cytosine; Cy1, *trans*-amino−oxy cytosine; Cy2, *cis*-amino−oxy cytosine; Cy3, *trans*-imino−oxo cytosine; Cy4, *cis*-imino−oxo cytosine; Me-Cy0, N_1-methyl amino−oxo cytosine;

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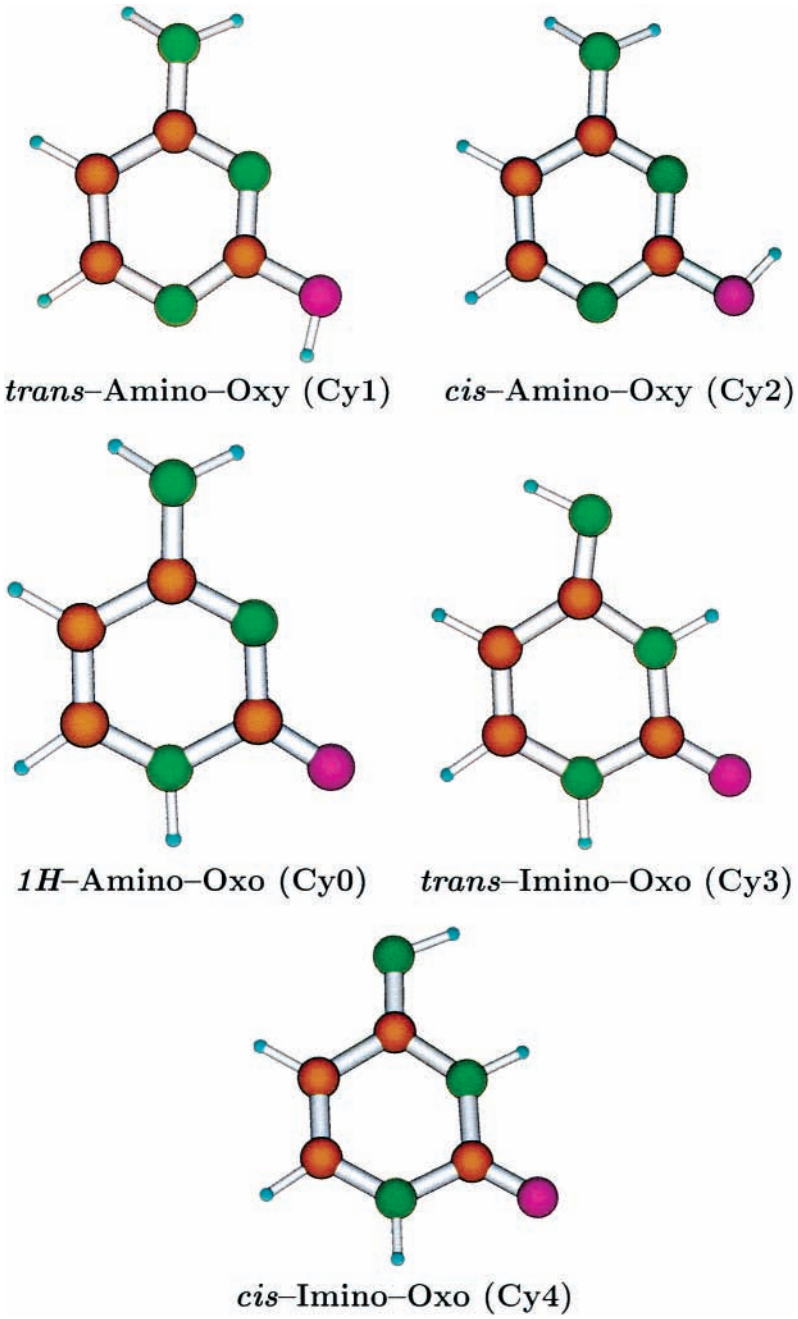

Figure 1. Lowest tautomers of cytosine.

TABLE 1: Tautomerization Energies (kcal/mol)

cytosine		N_1-methyl cytosine	
tautomer	ΔE	tautomer	ΔE
Cy1	0		
Cy2	0.73		
Cy0	2.28	Me-Cy0	0
Cy3	2.94	Me-Cy3	1.78
Cy4	4.67	Me-Cy4	3.54

Me-Cy3, N_1-methyl *trans*-imino−oxo cytosine; Me-Cy4, N_1-methyl *cis*-imino−oxo cytosine.

Cytosine. A number of bands are seen in the experimental spectrum of cytosine:[12,14,15] a narrow, structured band at ∼8.7−9.2 eV and two very wide ones, at ∼9.4−10.5 and ∼11.5−12.5 eV. A peak at ∼13.1−13.2 eV is followed by unresolved features starting from 14 eV. The following estimates were made in the experimental works cited above: π_1 at 8.82[12] or ∼9.0 eV,[14] n_1 at 9.45[12] or ∼9.8−10.0 eV,[14] π_2 at 9.90[12] or ∼9.8−10.0 eV,[14] n_2 at 11.8 eV,[12] and π_3 at 13.2 eV.[14] Reference 15 eliminated the possibility of a fourth ionization event under the second band envelope containing the second and the third ionizations. In a later work,[16] the spectrum of cytosine was reassigned on the basis of additional spectra on N_1-methylcytosine and the order of ionizations was suggested as follows: π_1 at 8.80 eV, n_1 and n_2 at ∼9.6−10.1 eV, π_2 at ∼9.8−10.3 eV, π_3 at 11.76 eV, and π_4 at 13.12 eV. Thus, the authors of ref 16 assigned three final states to one spectral band.

The present calculations indicate that the two amino−oxy forms of cytosine (Cy1 and Cy2) are isoenergetic and have the lowest energy. The amino−oxo (Cy0) and *trans*-imino−oxo (Cy3) forms are about 2 and 3 kcal/mol higher, respectively. While this order of tautomers is in agreement with preceding calculations,[18−21] it still cannot be considered definitive, for errors of 3 kcal/mol are not uncommon with the present methods.

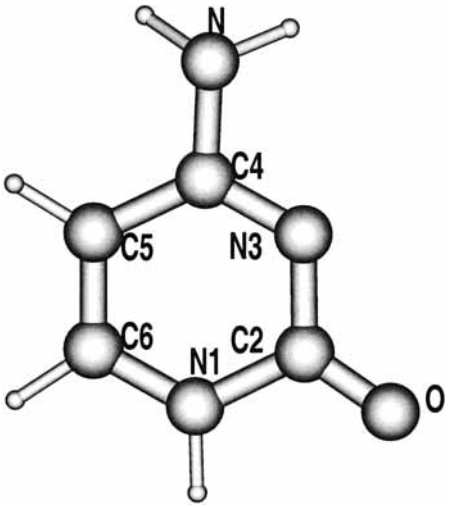

Figure 2. Numbering scheme in cytosine.

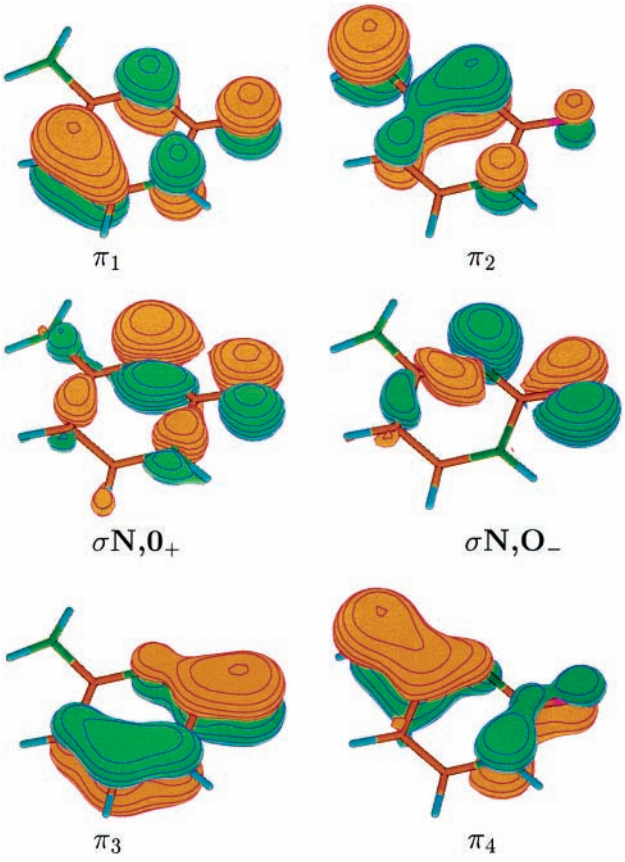

Figure 3. DOs of 1H-amino−oxo cytosine (Cy0).

1H-Amino−Oxo Form. The following ordering of ionization events is predicted by the P3 method for Cy0: π_1, π_2, n_1, n_2, π_3, π_4. Koopmans's theorem greatly overestimates IEs. Despite the presence of a number of heteroatoms, no Koopmans defects (misorderings of final states) are found for this tautomer.

All calculated values correspond very well with the experimental maxima obtained from ref 16 (see Table 2). The lowest cationic state is placed by P3 at 8.79 eV and corresponds to a π DO delocalized over all heavy atoms except for the amino group (see Figure 3). Only one binding pattern is revealed, that of C−C bonding in the ring. Electron density distribution in this DO is to some extent similar to those of the π_1 DOs in uracil and thymine.[27,28] The second ionization occurs from a π DO which presents a delocalized pattern of out-of-phase-lobes

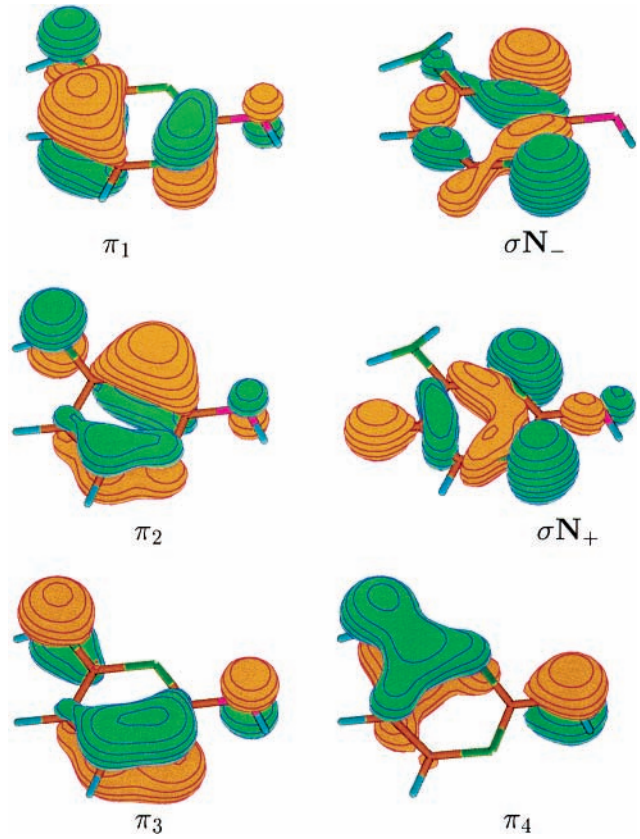

Figure 4. DOs of amino−oxy cytosine (Cy1).

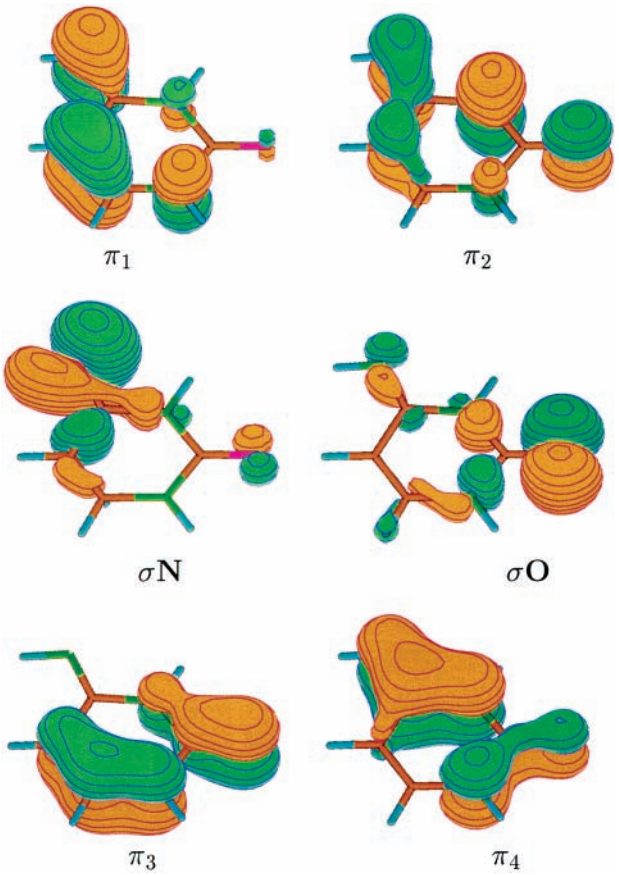

Figure 5. DOs of imino−oxy cytosine (Cy3).

with the highest amplitudes on the amino group's nitrogen and the adjacent C−N bond in the ring. Lobes on the remaining

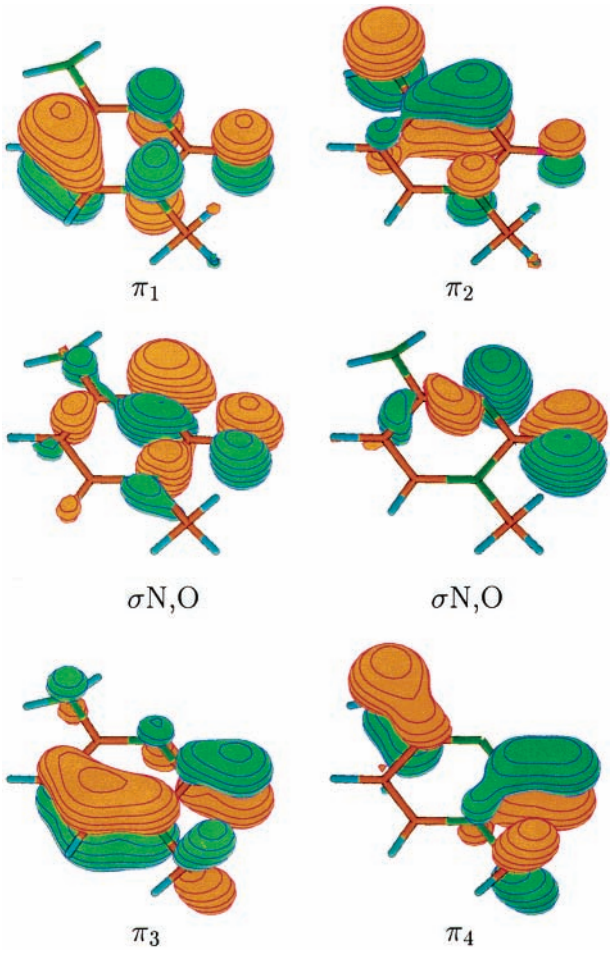

Figure 6. DOs of N_1-methyl amino−oxo cytosine (Me-Cy0).

TABLE 2: 1H-Amino−Oxo Cytosine IEs (eV)

MO	KT	P3	expt[12,14]	expt[16a]
π_1	9.30	8.79	∼8.7−9.2	8.80
π_2	10.55	9.54	∼9.4−10.5	9.8−10.3
n_1	11.35	9.64	∼9.4−10.5	9.6−10.1
n_2	12.05	9.96	∼9.4−10.5	9.6−10.1
π_3	13.35	12.08	∼11.5−12.2	11.76
π_4	14.53	13.02	∼13.2	13.12

[a] Estimated on the basis of Hartree−Fock, 4-31G calculations and comparisons with N_1-methyl cytosine PES.

nitrogen and on the carbonyl oxygen also contribute to the delocalization. The energy gap between the π_2 and the following n_1 (σN,O$^+$) is only 0.1 eV at the P3 level. This σN,O$^+$ DO is dominated by in phase n lobes on the pyrimidinic nitrogen and the carbonyl oxygen. The relative position of these two levels is different from that of uracil. There is a simple explanation for this distinction: the π_2 DO in cytosine is dominated by the antibonding conjugation of the amino group nitrogen lone pair and an adjacent three center bond in the ring. Such an interaction leads to a significant shift in the energy of this level. The next IE is predicted at 9.96 eV and pertains to another σN,O DO. The three, close-lying energies explain the complicated structure of the second ionization band in the experimental PES of cytosine.[12,14] Positions of the next two levels are predicted at 12.08 and 13.02 eV, while assignments made on the basis of comparison with the PES of N_1-methylcytosine in ref 16 give 11.76 and 13.12 eV, respectively.

Amino−Oxy Forms. Table 3 presents IEs of two amino−oxy tautomers of cytosine. As in the previous case, P3 gives

TABLE 3: Amino−Oxy Cytosine IEs (eV)

	Cy1		Cy2		
MO	KT	P3	KT	P3	expt[12,14]
π_1	9.27	8.93	9.23	8.91	∼8.7−9.2
σN$^-$	11.33	9.70	11.31	9.66	∼9.4−10.5
π_2	10.76	10.01	10.90	10.15	∼9.4−10.5
σN$^+$	13.22	11.41	13.25	11.45	∼11.5−12.2
π_3	13.10	11.72	13.05	11.66	∼11.5−12.2
π_4	14.93	13.22	14.99	13.26	∼13.2

excellent agreement between theoretical and observed peak positions. The P3 values and DOs differ little for the two rotamers, so only *trans*-amino−oxy cytosine data will be discussed here. The order of ionization events is π_1, n_1, π_2, n_2, π_3, π_4, which differs from that of Cy0. The first IE is only about 0.1 eV higher than in the case of Cy0. The values of 8.93 and 8.91 eV obtained by P3 for amino−oxy forms fit well into the observed envelope of 8.7−9.2 eV. Proton transfer from N_1 to the oxygen atom significantly changes the π_1 DO pattern (Figure 4). Most of the electron density is localized in the ring as two out-of-phase binding π lobes and significant participation by the amino group nitrogen appear. The second ionization occurs from an out-of-phase combination of nitrogen lone pairs delocalized into the ring. P3 places this event at 9.70 and 9.66 eV, respectively, for trans and cis forms of amino−oxy cytosine. These values are well within the second experimental band. The π_2 IEs are predicted at 10.01 and 10.15 eV. Both values fit into the same experimental band at ∼9.4−10.5 eV. The corresponding DO is dominated by an antibonding pattern of two, three center π fragments in the ring. Contribution from the amino nitrogen is less pronounced than in the case of the amino−oxo form, Cy0. The energy gap between the π_2 and the next n_2 level is about 1.4 eV. Thus, in the case of the amino−oxy cytosine tautomers, only two ionizations can be placed under the second experimental ionization band.[12,14] The n_2 levels are placed at 11.41 and 11.45 eV. These values are on the lower energy wing of the third experimental ionization band and can be assigned to its lowest-energy shoulder.[14] The n_2 DO displays an in phase combination of pyrimidinic nitrogen lone pairs (σN$^+$). The third experimental ionization band has the most complicated structure of all bands in the PES of cytosine.[12,14] There is another shoulder to the left of the main peak, which can be assigned to ionization from the π_3 levels of Cy1 and Cy2. The P3 IEs are 11.72 and 11.66 eV, respectively. The corresponding DOs are characterized by antibonding interactions between a large, four center lobe in the ring and p functions on the amino nitrogen and on the oxygen atom. The last ionization event under consideration occurs from the π_4 level and is placed by P3 at 13.22 and 13.26 eV. These values are in excellent agreement with the experimental peak position at ∼13.2 eV.

Imino−Oxo Forms. The imino−oxo forms of cytosine are the most biologically important tautomers of cytosine. When the N_1 position is bound to a sugar (as in the nucleotide cytidine) amino−imino tautomerism occurs, but oxo−oxy tautomerism does not. The lowest of imino−oxy forms, Cy3, is only 0.7 kcal/mol above amino−oxo cytosine (see Table 1). Its rotamer, Cy4, is about 1.7 kcal/mol higher.

P3 IEs of imino−oxo cytosines are summarized in Table 4 together with the experimentally observed band positions. The following order of ionizations is predicted for both trans and cis imino−oxo cytosines: π_1, π_2, n_1, n_2, π_3, and π_4. The positions of the first ionization event, at 8.83 and 8.81 eV, are very close to that of the amino−oxo form. The corresponding DO is dominated by the antibonding interaction of two, two center binding π lobes localized at the C═C bond in the ring

TABLE 4: Imino−Oxo Cytosine IEs (eV)

	Cy3		Cy4		
MO	KT	P3	KT	P3	expt[12,14]
π_1	9.23	8.83	9.16	8.81	∼8.7−9.2
π_2	10.80	9.78	10.95	9.93	∼9.4−10.5
σN	11.94	10.13	11.90	10.07	∼9.4−10.5
σO	12.63	10.65	12.95	10.97	∼11[a]
π_3	13.97	12.65	13.94	12.60	∼12.6[b]
π_4	14.37	12.95	14.44	13.02	∼13.2

[a] A low-intensity feature. [b] One of the many shoulders to the right of the main peak at 12 eV.

and the C═N bond of the imino group. Significant input from a N_1 p function also occurs (see Figure 5). The following ionization state is also of the π type and is predicted by P3 to occur at 9.78 and 9.93 eV. These energies are higher than the π_2 IE in the case of the amino−oxo form but are still within the second ionization band. The corresponding DOs are delocalized over the entire molecule and include a four center (three center in the case of Cy4) binding π fragment in antibonding interaction with a p orbital on N_3. Ionization from the first nonbonding level follows, and its energies are placed at 10.13 and 10.07 eV, respectively, for Cy3 and Cy4. The n_1 DO is mostly localized on the iminic nitrogen. The next n_2 IE is predicted at 10.65 eV for Cy3 and at 10.97 eV for Cy4. There are no obvious features in the experimental spectrum corresponding directly to these energies although a low-amplitude structure can be discerned between the second and the third bands[14] at about 11 eV. The n_2 DO of Cy3 is dominated by a lobe at the carbonyl oxygen with some density delocalized into the ring atoms. For Cy4, substantial in-phase participation by a lone pair lobe at the imino group leads to a ∼0.3 eV hipsochromic shift of the n_2 level. The π_3 IE is predicted at 12.65 and 12.60 eV and might correspond to one of the numerous shoulders on the high-energy wing of the third experimental ionization band. The π_3 DO resembles its Cy0 counterpart. The last ionization event under consideration occurs from the π_4 level and is placed at 12.95 and 13.02 eV by the P3 calculations. These values agree reasonably well with the experimental peak at ∼13.2 eV.[14]

Cytosine Summary. Table 5 summarizes all P3 results on IEs of cytosine tautomers. The first IEs of all five tautomers are very close to each other and to the observed band maximum at 8.80 eV.[14,16] This means that in the case of cytosine, the first ionization event is hardly influenced by tautomerization. Many ionization events can be found in the energy region covered by the second band: three ionizations from the amino−oxo cytosine, two ionizations from each of the imino−oxo tautomers, and two ionizations from both amino−oxy forms. Ionization from the n_2 levels of the imino−oxo forms are to the extreme right of the second band and might not even be seen in the spectrum. It is still difficult to define a single, dominant ionization that would define the main peak position of this band as there are at least four ionization events close to 10.0 eV. The third experimental band may contain seven ionizations varying in energies from ∼11.4 to ∼12.6 eV. It is likely that the main peak observed at 11.76 eV cannot be explained by ionization from the π_3 level of the amino−oxo cytosine. The most probable sources for this maximum are ionizations from the π_3 levels of two amino−oxy tautomers, Cy1 and Cy2. The shoulders to the left of this maximum are most likely due to ionizations from the n_2 levels of the same tautomers, while the structures to the right may be provided by the π_3 ionizations from all three oxo forms. The fourth band at ∼13.0−13.5 eV is defined by ionizations from the π_4 levels. All IEs are rather close to each other and to the experimental peak position at ∼13.12 eV.[16]

TABLE 5: Summary of Cytosine IEs (eV)

expt[14]	P3	MO	tautomer
∼8.7−9.2	8.79	π_1	Cy0
	8.91	π_1	Cy2
	8.93	π_1	Cy1
	8.81	π_1	Cy4
	8.83	π_1	Cy3
∼9.4−10.5	9.54	π_2	Cy0
	9.64	n_1	Cy0
	9.96	n_2	Cy0
	9.66	n_1	Cy2
	9.70	n_1	Cy1
	9.78	π_2	Cy3
	9.93	π_2	Cy4
	10.01	π_2	Cy1
	10.15	π_2	Cy2
	10.07	n_1	Cy4
	10.13	n_1	Cy3
	10.65	n_2	Cy3
	10.97	n_2	Cy4
∼11.5−12.5 eV	12.08	π_3	Cy0
	11.41	n_2	Cy1
	11.45	n_2	Cy2
	11.66	π_3	Cy2
	11.72	π_3	Cy1
	12.65	π_3	Cy3
	12.60	π_3	Cy4
∼13.0−13.5	13.02	π_4	Cy0
	12.95	π_4	Cy3
	13.02	π_4	Cy4
	13.22	π_4	Cy1
	13.26	π_4	Cy2

TABLE 6: N_1-Methyl Amino−Oxo Cytosine IEs (eV)

MO	KT	P3	expt[16]
π_1	9.07	8.53	8.65
π_2	10.37	9.32	∼9.5−10.0
n_1	11.27	9.54	∼9.5−10.0
n_2	11.94	9.78	∼9.5−10.0
π_3	13.03	11.78	11.53
π_4	14.02	12.56	12.40

N_1-Methyl Cytosine. Bands in the PES of N_1-methylcytosine[14,16] are better resolved and less complicated than those of cytosine. The envelopes that are seen are as follows: a sharp, narrow band from ∼8.4 to 8.9 eV with the maximum at 8.65 eV; a wide, structured band between ∼9.2 and 10.6 eV; and two well-resolved bands with maxima at 11.53 and 12.40 eV.[14,16] As was the case with cytosine, the earlier work placed two ionization events under the second band while in the latter publication three ionizations were assigned into this range of IEs. With methylation at the N_1 position, the number of low-lying tautomers is reduced to three. These are the amino−oxo form and two imino−oxo forms. In all cases, the lowest energy isomers were those with the cis orientation of methyl groups. (The cis orientation of a methyl group at N_1 in pyrimidines denotes an in-plane methyl hydrogen in a cis position with respect to the C_6 hydrogen.) Optimization with the 6-311G** basis gave the following order of tautomers: amino−oxo < *trans*-imino−oxo < *cis*-imino−oxo (see Table 1). Calculated and experimental IEs are gathered in Tables 6 and 7. DO plots are shown in Figures 6 and 7.

Amino−Oxo Form. The following order of ionizations is predicted by P3 for the amino−oxo form of *cis*-N_1-methylcytosine: π_1, π_2, n_1, n_2, π_3, and π_4. The first ionization event is

TABLE 7: Imino−Oxo N_1-Methyl Cytosine IEs (eV)

	Me-Cy3		Me-Cy4		
MO	KT	P3	KT	P3	expt[14,16]
π_1	8.96	8.49	8.90	8.46	∼8.4−8.9
π_2	10.69	9.62	10.85	9.78	∼9.5−10.0
n_1	11.84	10.00	11.81	9.94	∼9.5−10.0
n_2	12.55	10.51	12.86	10.82	∼10.5−10.7[1]
π_3	13.33	12.03	13.29	11.99	
π_4	14.09	12.78	14.14	12.82	

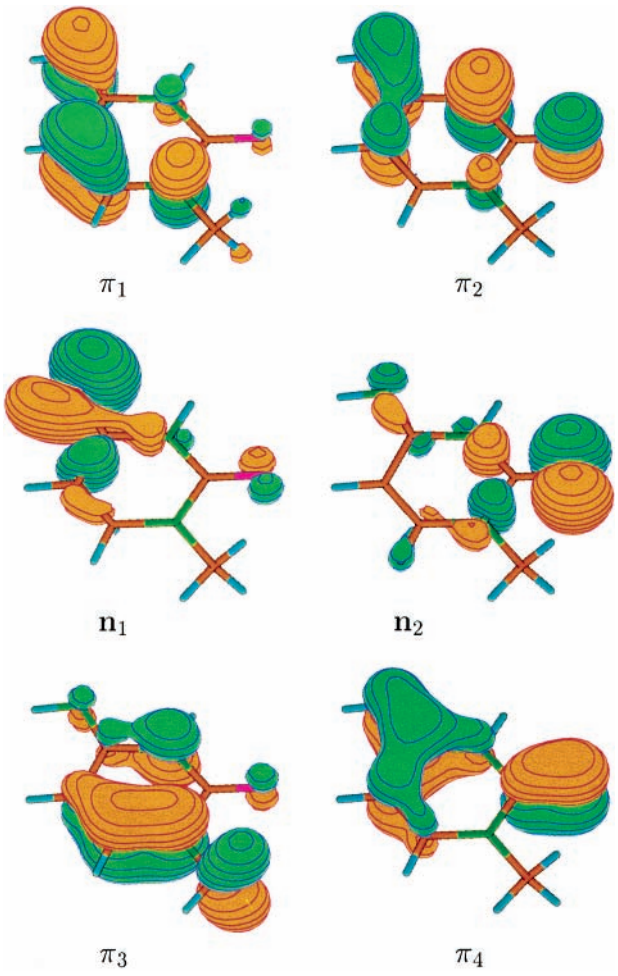

Figure 7. DOs of N_1-methyl imino−oxo cytosine (Me-Cy3).

predicted at 8.53 eV. This value is in good agreement with the experimental peak position at 8.65 eV. With close to no contribution from the methyl group, the corresponding DO does not differ much from that of amino−oxo cytosine. The position of the next π_2 IE is predicted at 9.32 eV, which is about 0.4 eV lower than the observed peak at ∼9.7 eV. In the range of energies under consideration, the P3 method is very unlikely to give so large a deviation. Close examination of the PES[14,16] reveals a smaller peak to the left of the main one at 9.7 eV. Thus, ionization from the π_2 level in N_1-methyl amino−oxo cytosine may be assigned to this smaller peak while the main one could be the result of some other ionization event pertaining to the amino−oxo form or another tautomer. Two ionizations from nonbinding levels follow, and these are placed at 9.54 and 9.78 eV. Both values fit well into the observed feature at ∼9.5−10.0 eV and might be responsible for the peak at ∼9.7 eV. There are no contributions from the CH_3 group in either of the corresponding DOs (see Figure 6); therefore, energy shifts with respect to Cy0 are small. The position of the next π_3 level is predicted at 11.78 eV, while the experimental peak position is at 11.53 eV. Comparison with π_3 of Cy0 (12.08 eV) reveals a significant hipsochromic shift. Two notable contributions from methyl and amino groups appear in the π_3 DO of N_1-methylcytosine (compare Figures 3 and 6). Even bigger changes in the electron density distribution can be noted in the case of the π_4 DO. Here, the presence of the methyl group at N_1 leads to redistribution in the N_1C_2O binding lobe. The corresponding IE is 12.56 eV (the experimental peak position is 12.40 eV[16] as compared with 13.02 eV in unsubstituted amino−oxo cytosine).

Imino−Oxo Forms. Two imino−oxo forms of N_1-methylcytosine are close in energy to the main, amino−oxo form, although the differences are larger than in the case of unsubstituted tautomers (see Table 1). The order of ionization events predicted by P3 in trans and cis imino−oxo forms is the same as in amino−oxo N_1-methylcytosine. The first ionization is from the π_1 level and is placed at 8.49 eV and at 8.46 eV for trans and cis tautomers, respectively. These energy values fit well into the observed range of ∼8.4−8.9 eV.[14,16] Ionization from the π_2 level follows, and the P3 energies, 9.62 and 9.78 eV, also correspond very well to the observed band at ∼9.5−10.0 eV. Both π DOs are delocalized over the entire molecule and significant participation of the imino group nitrogen can be seen (see Figure 7). The next ionization level is n_1, and its position is predicted at 10.00 and 9.94 eV for trans and cis forms. The same experimental band as above contains n_1 ionizations. The corresponding DO can be described as an out-of-phase combination of lone pair functions at the imino nitrogen and carbonyl oxygen atoms. The DO is significantly delocalized. Unlike the case of the amino−oxo form, the next nonbonding level is a bit lower. The n_2 IEs are 10.51 eV for the trans form and 10.82 eV for the cis form. In both forms, the n_2 DOs comprise combinations of lone pair functions at the carbonyl oxygen and imino nitrogen. These values coincide with a shoulder seen at ∼10.5−10.7 eV. An appreciable difference in the n_2 energies between the two imino forms can be attributed to much smaller participation of imino nitrogen in the case of the cis form. The last two ionizations are of the π type. P3 predicts ionization from the π_3 level at 12.03 and 11.99 eV while ionizations from the π_4 are placed at 12.78 and 12.82 eV, respectively, for trans and cis forms. Although there are no resolved experimental peaks that would correspond to either of these theoretical values, all P3 energies do fit under the envelopes at ∼11.5−12.2 and 12.5−13.2 eV seen in Figure 1 of ref 14.

Conclusions

Electron propagator calculations in the P3 approximation provide assignments that are consistent with photoelectron spectra. The order of cationic final states is π_1, π_2, n_1, n_2, π_3, π_4 for all tautomers except for the amino−oxy forms of cytosine, where the order is π_1, n_1, π_2, n_2, π_3, π_4.

Each of the five cytosine isomers has a calculated π_1 IE that is close to the lowest experimental peak. The broader second feature seen in PES is produced by π_2, n_1, and n_2 final states belonging to several tautomers. In the third peak, π_3 final states from many isomers, as well as n_2 contributions from amino−oxy tautomers are represented. Ionizations pertaining to the π_4 final states are responsible for the fourth feature in the PES. DOs corresponding to these IEs are, in general, delocalized over the entire nuclear framework.

For 1-methylcytosine, the first peak in the PES is assigned to a π_1 hole state. The broader, second feature contains the π_2, n_1, and n_2 IEs of the amino−oxo isomer as well as the π_2 and

n_1 IEs of the imino−oxo forms. In the latter isomers, the n_2 hole is assigned to a shoulder on the second peak. The third and fourth peaks correspond to π_3 and π_4 IEs.

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