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Vertical Ionization Energies of Adenine and 9-Methyl Adenine[†]

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Vertical ionization energies of 9-H adenine and 9-methyl adenine have been calculated with the following, ab initio, electron propagator methods: the outer valence Green's function (OVGF), partial third-order theory (P3), and the third-order algebraic diagrammatic construction, or ADC(3). Basis set effects have been systematically examined. All methods predict near degeneracy in the π_2-n_1 and π_3-n_2 pairs of cationic, adenine final states and larger splittings of the corresponding, cationic states of 9-methyl adenine. P3 results for adenine predict the following order of the first six final states: π_1, n_1, π_2, n_2, π_3, n_3. Coupled-cluster calculations on the first three cationic states of adenine confirm these predictions. OVGF and ADC(3) calculations reverse the order of the second and third states and of the fourth and fifth states. All results confirm previous interpretations of experiments in which the second and third spectral bands correspond to the aforementioned pairs of final states and disagree with a recent reassignment based on time-resolved photoelectron spectra. Lower ionization energies and larger splittings in the methylated molecule are interpreted in terms of phase relationships in the Dyson orbitals. ADC(3) results confirm the qualitative validity of the one-electron approximation for the first six final states of both molecules and disclose its inadequacies for higher ionization energies.

Introduction

Electronic processes in genetic matter such as DNA, RNA, and their building blocks have fundamental importance in biology and biochemistry. Ionization phenomena in nucleic acid bases (NABs) have been extensively studied both experimentally[1−7] and computationally at high levels of theory.[8−16] Electron propagator calculations of the vertical ionization energies (IEs) of guanine and cytosine tautomers[9−11] permitted assignment of ultraviolet (UV) photoelectron spectra (PES). Analogous descriptions of thymine and other substituted uracils[12] provided a qualitative picture of the intrinsic electronic effects of methylation upon ionization processes. Experimental UV PES of guanine and cytosine were difficult to interpret because of the possible presence of energetically close tautomers in the gas phase.[2,3] For uracil[5] and adenine,[6] such a problem did not exist, for these NABs do not have low-energy isomers that are experimentally relevant.[17,18] However, in the UV PES of adenine, peaks corresponding to ionizations from the π_2 and n_1 levels and the π_3 and n_2 levels could not be resolved. A peak at ∼9.6 eV was assigned to ionizations from the π_2 and n_1 levels and another at ∼10.5 eV was assigned to ionizations from the π_3 and n_2 levels. Electron propagator calculations in the partial third-order approximation (P3)[19] confirmed the proximity of these levels.[13]

In a set of recent works, angle-resolved PES (ARPES) of uracil, methyl uracils, 5-halo uracils, and adenine obtained with synchrotron radiation were reported.[14−16] According to these assignments, the π_2 and n_1 levels of adenine differed by 0.09 eV, whereas the energy difference between the π_3 and n_2 levels was only 0.06 eV. (See Table 1.) On the basis of observed asymmetry parameters, the order of the first five final states was given as π_1, n_1, π_2, n_2, π_3. The first spectral band was assigned to the π_1 final state. Two states were assigned to each of the following two bands. Electron propagator calculations performed in support of the experiments permuted the order of states to π_1, π_2, n_1, π_3, n_2.[16]

TABLE 1: Experimental and Theoretical Vertical IEs of Adenine, eV

MO	UV PE[6]	ARPES[16]	TRPES[20]	P3[a13]	OVGF[b16]	CASPT2[c25]
π_1	8.48	8.47	∼8.5	8.49	8.32	8.37
n_1	∼9.6	9.45	∼9.6	9.45	9.45	9.05
π_2	∼9.6	9.51	∼10.5	9.56	9.40	9.54
n_2	∼10.5	10.45	∼10.5	10.48	10.53	9.96
π_3	∼10.5	10.51		10.50	10.50	10.38
n_3	11.39	11.35		11.54	11.61	11.06
π_4	12.10	12.09		12.15	12.28	
π_5	13.21	13.20		13.46	13.63	

[a] 6-311G** basis. [b] 6-311++G** basis. [c] ANO basis.

A different assignment was presented in a recent publication in which time-resolved photoelectron spectra (TRPES) of adenine and 9-methyl adenine were recorded.[20] In these experiments, a molecule is first promoted to its second, excited singlet state, S_2, which, for adenine, is considered to have $\pi-\pi^*$ character. This state relaxes subsequently into an S_1, $n-\pi^*$ state. PES of these excited states are obtained separately by introducing time delays between the excitation and the subsequent ionization events. Features in these spectra were assigned to vertical IEs of the molecule's ground state. TRPES IEs of ref 20 are presented in the fourth column of Table 1. The first IE (that is, for the π_1 final-state) and the second IE (that of the n_1 state) correspond to the assignments of refs 6 and 16. So does the ionization from the n_2 level which is placed at ∼10.5 eV. Because no π level ionization was found in the vicinity of ∼9.6 eV, the π_2 ionized state was placed at ∼10.5 eV. No higher IEs were presented. Assignments also were made for 9-methyl adenine.

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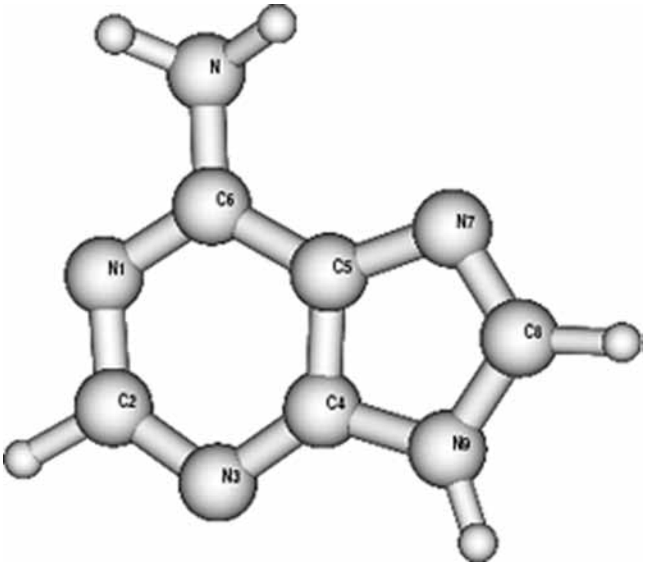

Figure 1. Molecular structure of 9H-Adenine.

A summary of recent, computational results on vertical IEs of adenine is given in Table 1. The P3 electron propagator IE values[13] obtained with the 6-311G** basis[21] seem to be in closest agreement with the experimental IEs of refs 6 and 16. The outer valence Green's function (OVGF)[22] IEs[16] obtained with the more flexible 6-311++G** basis[23] are only slightly different from the P3/6-311G** values. Energy differences between the two pairs of levels ($n_1-\pi_2$ and $n_2-\pi_3$) are well within the precision limits of these electron propagator methods. IEs obtained with the third-order algebraic diagrammatic construction or ADC(3) method[22,24] and the 6-31G basis also were published in ref 16. Although the absolute values contrast with P3, OVGF, and experimental IEs, the sequence of states (except for the two quasi-degenerate pairs) is the same.

Recent calculations[25] were performed with the CASPT2 method[26,27] and (C,N,O)[4s3p1d]/(H)[2s1p] contracted atomic natural orbital basis sets. Whereas the CASPT2 IEs of π levels differ from the experimental values by 0.05−0.18 eV for uracil, thymine, adenine and guanine, the results for n levels differ by 0.30−0.57 eV. The largest deviations were obtained for purine NABs, adenine and guanine.

In this report, we present IEs of adenine obtained with various electron propagator methods[22,24,28−31] and basis sets of increasing flexibility. The coupled-cluster singles and doubles approximation (CCSD)[32] also has been employed. Because methylation is a crucial step in a variety of processes that govern the transmission of genetic information and is likely to affect the reactivity of NABs, the effects of a CH_3 substituent at the 9 position (see Figure 1) on IEs are determined computationally and are analyzed in terms of Dyson orbital amplitudes.

Methods

Theory. For each vertical IE calculated with electron propagator methods,[28−31] there corresponds a Dyson orbital defined by

$$\varphi^{\mathrm{Dyson}}(x_1) = N^{-1/2} \int \Psi^*_{\mathrm{cation}}(x_2, x_3, x_4, ..., x_N) \times \Psi_{\mathrm{molecule}}(x_1, x_2, x_3, ..., x_N)\mathrm{d}x_2\mathrm{d}x_3\mathrm{d}x_4...\mathrm{d}x_N$$

TABLE 2: P3, OVGF, and ΔCCSD IEs of Adenine

	6-311++G**						
MO	KT	P3	OVGF/A	OVGF/B	OVGF/C	ΔCCSD	ref 6
π_1	8.49	8.52	8.15(0.90)	8.19(0.90)	8.32(0.90)	8.27	8.48
π_2	10.21	9.64	9.35(0.89)	9.40(0.89)	9.51(0.89)	9.53	~9.6
n_1	11.20	9.52	9.35(0.89)	9.45(0.89)	9.55(0.89)	9.43	~9.6
π_3	11.61	10.58	10.40(0.89)	10.49(0.88)	10.59(0.88)		~10.5
n_2	12.34	10.55	10.42(0.88)	10.53(0.88)	10.62(0.89)		~10.5
n_3	13.54	11.56	11.49(0.88)	11.61(0.88)	11.69(0.88)		11.39
π_4	13.60	12.32	12.20(0.86)	12.28(0.86)	12.37(0.86)		12.10
π_5	15.24	13.60	13.54(0.85)	13.63(0.86)	13.72(0.85)		13.21

TABLE 3: P3 and OVGF IEs of Adenine

	6-311++G(2df,2p)					
MO	KT	P3	OVGF/A	OVGF/B	OVGF/C	ref 6
π_1	8.45	8.68	8.22(0.90)	8.26(0.90)	8.42(0.90)	8.48
π_2	10.18	9.80	9.43(0.89)	9.48(0.88)	9.63(0.88)	~9.6
n_1	11.16	9.68	9.42(0.88)	9.55(0.88)	9.67(0.89)	~9.6
π_3	11.60	10.76	10.50(0.88)	10.60(0.88)	10.72(0.88)	~10.5
n_2	12.29	10.69	10.48(0.88)	10.62(0.88)	10.74(0.89)	~10.5
n_3	13.50	11.70	11.56(0.87)	11.70(0.88)	11.80(0.88)	11.39
π_4	13.59	12.45	12.27(0.86)	12.37(0.86)	12.49(0.86)	12.10
π_5	15.22	13.75	13.62(0.85)	13.72(0.85)	13.83(0.84)	13.21

where N is the number of electrons in the molecule and x_i is the space-spin coordinate of electron i. The Dyson orbital represents the change in electronic structure accompanying the detachment of an electron from a molecule. The pole strength (PS) associated with a given IE is related to the corresponding Dyson orbital by

$$P_{\mathrm{q}} = \int |\varphi_{\mathrm{q}}^{\mathrm{Dyson}}(x)|^2 \mathrm{d}x$$

PSs may vary between 0 and 1.

Two types of electron propagator approximations are commonly used. The OVGF and P3 approximations neglect off-diagonal elements of the self-energy matrix, where differential correlation and final-state orbital relaxation corrections are included, in the canonical, Hartree−Fock basis. Both of these methods involve the evaluation of third-order terms in the self-energy. In diagonal approximations, the Dyson equation has a simple form

$$E_{\mathrm{p}} = \epsilon_{\mathrm{p}} + \Sigma_{\mathrm{pp}}(E_{\mathrm{p}})$$

where the self-energy matrix is designated by $\sum(E)$ and ϵ_{p} is a canonical, Hartree−Fock orbital energy. PSs between 0.85 and unity indicate that one-electron descriptions of final states (e.g., via Koopmans's theorem) are qualitatively valid and that methods that assume a diagonal self-energy matrix such as OVGF are applicable.[22]

Nondiagonal self-energy methods, such as ADC(3),[24] are needed to describe final states in which the one-electron picture collapses. Here a Hermitian eigenvalue problem of the type

$$\mathbf{AY} = \mathbf{YE}$$

is solved. In the ADC(3) approximation, the basis of operators that defines **A** spans the 1 h, 1p, 2h1p, and 2p1h subspaces. The self-energy that is implicit in such calculations includes all third-order terms and certain types of terms (such as ring and ladder diagrams) in all orders.

Computations. All calculations were performed with the Gaussian-03 suite of programs.[33] Molecular structures of 9H-adenine and 9-methyl adenine were optimized with second-order

TABLE 4: Adenine P3 IEs, cc Bases

	cc-pVDZ		aug-cc-pVDZ		cc-pVTZ		aug-cc-pVTZ		cc-pVtrQZ	
MO	KT	P3	KT	P3	KT	P3	KT	P3	KT	P3
π_1	8.29	8.32	8.42	8.43	8.34	8.59	8.43	8.70	8.38	8.56
π_2	10.02	9.39	10.15	9.55	10.08	9.70	10.17	9.82	10.11	9.67
n_1	11.02	9.26	11.14	9.42	11.06	9.57	11.14	9.69	11.14	9.59
π_3	11.47	10.34	11.56	10.50	11.51	10.67	11.58	10.78	11.53	10.63
n_2	12.20	10.30	12.28	10.46	12.19	10.60	12.28	10.72	12.28	10.62
n_3	13.42	11.45	13.50	11.48	13.40	11.61	13.48	11.72	13.48	11.62
π_4	13.40	11.93	13.56	12.23	13.50	12.35	13.57	12.47	13.52	12.32
π_5	15.01	13.32	15.20	13.54	15.13	13.65	15.21	13.76	15.15	13.62
n_4			16.14	14.40	16.04	14.51	16.12	14.61	16.12	14.53

TABLE 5: Adenine OVGF IEs, cc Bases

	aug-cc-pVDZ OVGF			cc-pVTZ OVGF			cc-pVtrQZ OVGF			
MO	A	B	C	A	B	C	A	B	C	CASPT2[25]
π_1	8.11	8.25	8.34	8.13	8.13	8.31	8.13	8.16	8.32	8.37
π_2	9.34	9.48	9.54	9.33	9.35	9.51	9.32	9.37	9.51	9.54
n_1	9.36	9.54	9.58	9.30	9.42	9.55	9.36	9.48	9.54	9.05
π_3	10.42	10.59	10.63	10.40	10.49	10.61	10.40	10.50	10.60	10.38
n_2	10.44	10.62	10.66	10.38	10.50	10.62	10.43	10.55	10.66	9.96
n_3	11.51	11.69	11.72	11.45	11.58	11.70	11.50	11.63	11.73	11.06
π_4	12.22	12.37	12.42	12.17	12.24	12.37	12.17	12.36	12.37	

TABLE 6: Adenine Second-Order IEs

	electron propagator second order				CASPT2[25]
MO	6-311++G**	cc-pVTZ	cc-pVtrQZ	aug-cc-pVDZ	ANO/431/21
π_1	8.01	8.07	8.03	7.91	8.37
π_2	8.99	9.05	8.99	8.88	9.54
n_1	8.28	8.34	8.34	8.19	9.05
π_3	9.82	9.91	9.85	9.74	10.38
n_2	9.33	9.38	9.38	9.24	9.96
n_3	10.34	10.41	10.41	10.28	11.06
π_4	11.59	11.65	11.60	11.51	
π_5	12.83			12.75	

TABLE 7: Adenine ADC(3) IEs

state	6-311G** ADC(3)	6-311++G** ADC(3)	6-311G(2df) ADC(3)	aug-cc-pVDZ ADC(3)
π_1	8.16(0.89)	8.34(0.88)	8.23(0.88)	8.33(0.88)
π_2	9.45(0.87)	9.63(0.87)	9.53(0.87)	9.62(0.87)
n_1	9.59(0.88)	9.78(0.88)	9.68(0.88)	9.77(0.88)
π_3	10.49(0.86)	10.65(0.86)	10.58(0.86)	10.66(0.86)
n_2	10.62(0.88)	10.81(0.88)	10.70(0.88)	10.80(0.87)
n_3	11.65(0.86)	11.84(0.86)	11.73(0.86)	11.83(0.86)
π_4	12.18(0.70)	12.35(0.69)	12.24(0.66)	
	12.74(0.12)	12.88(0.13)	12.72(0.14)	12.82(0.14)
	13.95(0.02)			
π_5	13.56(0.58)			
	13.76(0.13)			

perturbation theory (MP2) and the 6-311G** basis.[21] Harmonic frequency analysis confirmed the determination of minima for both optimized structures. Adenine and its methyl derivative have decidedly nonplanar structures. Vertical IEs were calculated with propagator methods. The results in electronvolts are compiled in Tables 2−10. The tables also contain the Koopmans's theorem IE values (KT). Application of a procedure that chooses the most reliable of the three OVGF results[34] produces the so-called recommended value. In Tables 2, 3, 5, 8 and 9, the B procedure is recommended for all final states except for the first, where the C value is preferred.

Two kinds of basis sets were involved in the propagator calculations: the 6-311G type[21,23] and the correlation-consistent type,[35] that is aug-cc-pVDZ, cc-pVTZ, aug-cc-pVTZ, and cc-pVQZ. In the last case, g and f functions for C and N and d functions for H were omitted; the latter, truncated basis will be designated as cc-pVtrQZ.

Results and Discussion

Adenine P3 and OVGF IEs. ***Improvements on 6-311G** Bases.*** Previous P3 and OVGF IEs of 9H-adenine obtained with the 6-311G** basis[13] are listed in Table S1 of Supporting Information. It is clear that the P3 results are closer to the experimental energies than any of the OVGF/6-311G** data. This trend is especially pronounced for the first two OVGF IEs pertaining to π levels. Relative positions of the π_2 and n_1 levels are inverted from P3 to OVGF, whereas the π_3 and n_2 levels remain almost degenerate.

The 6-311G** basis was extended by inclusion of diffuse functions on all atoms (Table 2). The P3 IEs increased in general but did not change much. The lower-lying π levels, π_4 and π_5, underwent the largest changes. The one-electron picture of ionization is not valid for these two levels.[13] On the other hand, the OVGF IEs improved markedly upon inclusion of diffuse functions (see Table 2). The energetic proximity of the $\pi_2-\mathrm{n}_1$ and $\pi_3-\mathrm{n}_2$ pairs was retained. Table 2 also contains ΔCCSD values of vertical IEs of 9H-adenine. These values are very close to the electron propagator IEs. ΔCCSD IEs for the π_2 and n_1 levels in 9H-adenine show the same trend as their electron propagator counterparts; the two levels are very close. Convergence failures in unrestricted Hartree−Fock calculations prevented the generation of ΔCCSD results for final states with n_2 and π_3 holes.

Table 3 contains the P3 and OVGF IEs obtained with basis sets with additional polarization functions. Changes with respect to the 6-311++G** results of Table 2 results are less than 0.2 eV. The separations between the π_1 level and the two pairs of almost-degenerate states are conserved.

Basis set improvements on P3/6-311G**[13] and OVGF/6-311++G**[16] calculations lead to larger predicted IEs. The best P3 results of Table 3 produce the same ordering of final states (π_1, n_1, π_2, n_2, π_3, n_3) as that of ref 13. They also are consistent with the assignment of these states to the first four bands in the ARPES experiments.[16] OVGF/6-311++G** results of ref 16 and Table 2 reverse the ordering of states within each of the

TABLE 8: 9-Methyl Adenine 6-311++G IEs**

			OVGF				
MO	KT	P3	A	B	C	UV PES[6]	TRPES[20]
π_1	8.38	8.37	8.01	8.04	8.17	8.39	~8.4
π_2	9.98	9.36	9.07	9.11	9.23	~9.4	~10.2
n_1	11.13	9.49	9.31	9.41	9.51	~9.4	~9.4
π_3	11.21	10.11	9.94	10.03	10.13	~10.2	
n_2	12.23	10.41	10.28	10.39	10.48	~10.2	~10.2
n_3	13.31	11.38	11.29	11.40	11.49	11.16	
π_4	13.53	12.18	12.08	12.17	12.26	11.93	
π_5	14.65	13.18	13.15	13.25	13.32	12.81	

TABLE 9: 9-Methyl Adenine cc-pVtrQZ IEs

			OVGF				
MO	KT	P3	A	B	C	UV PES[6]	TRPES[20]
π_1	8.27	8.42	7.99	8.03	8.18	8.39	~8.4
π_2	9.89	9.40	9.05	9.10	9.24	~9.4	~10.2
n_1	11.08	9.58	9.35	9.46	9.58	~9.4	~9.4
π_3	11.14	10.16	9.92	10.02	10.13	~10.2	
n_2	12.17	10.48	10.30	10.42	10.53	~10.2	~10.2
n_3	13.26	11.44	11.30	11.43	11.53	11.16	
π_4	13.45	12.21	12.06	12.16	12.26	11.93	
π_5	14.58	13.21	13.13	13.23	13.32	12.81	

π_2−n_1 and π_3−n_2 pairs with the π IE being lower in both cases and the order of final states becoming π_1, π_2, n_1, π_3, n_2, n_3. Both sets of calculations agree on the assignment of the second (B) band to the π_2 and n_1 final states and the assignment of the third (C) band to the π_3 and n_2 final states. They also agree that each of the first four bands should be separated by approximately 1 eV. Similar conclusions with respect to the A and B bands follow from the ΔCCSD results of Tables 2 and 3.

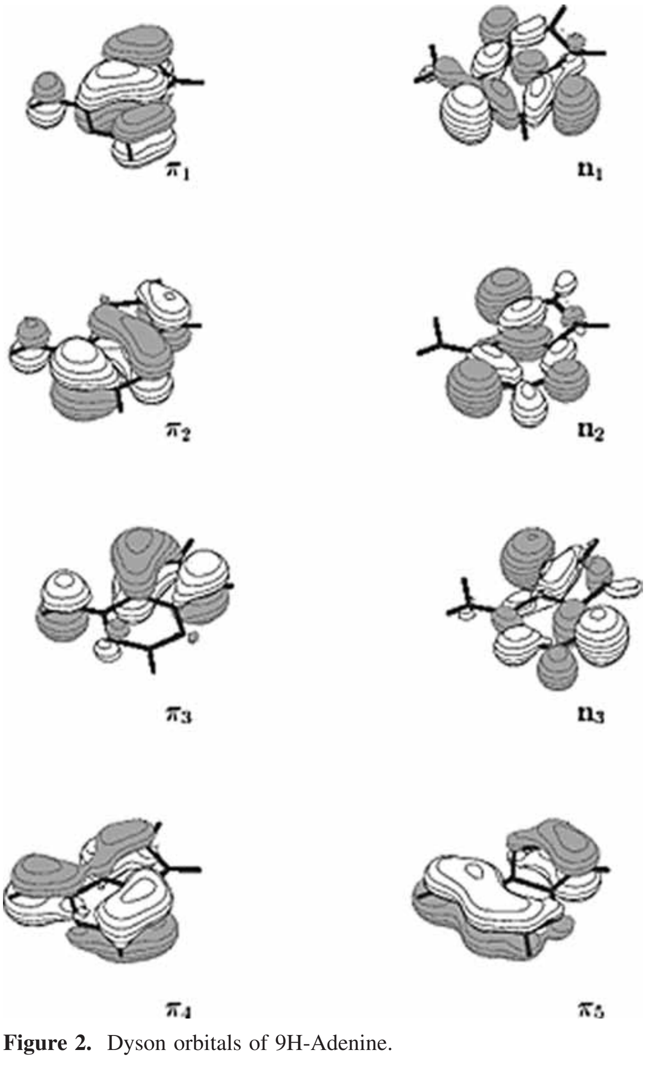

Figure 2. Dyson orbitals of 9H-Adenine.

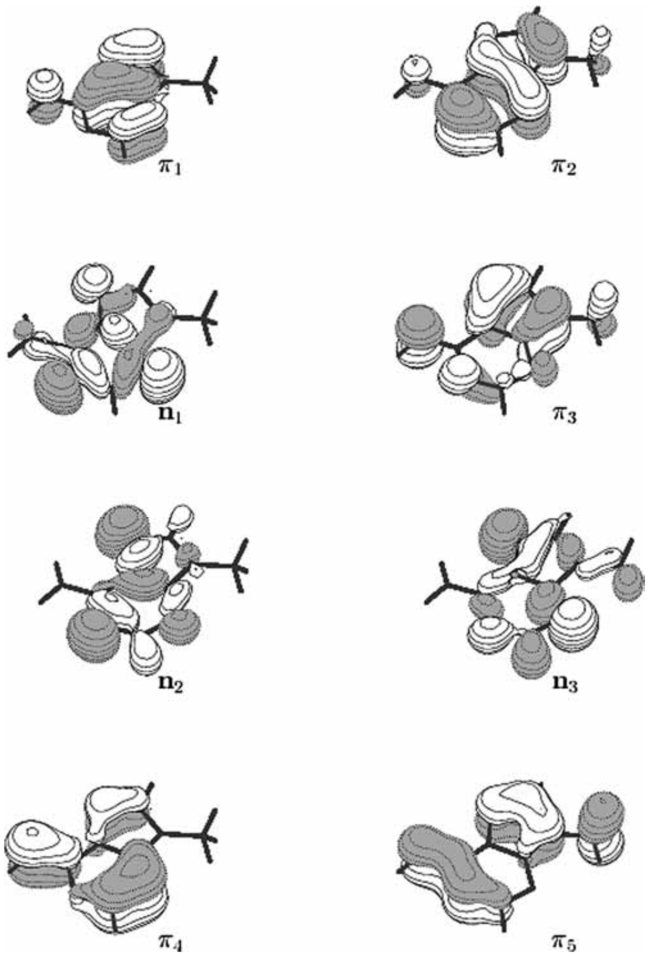

Figure 3. Dyson orbitals of 9-Methyl Adenine.

Correlation-Consistent Bases. P3 IEs obtained with various correlation-consistent basis sets are presented in Table 4. The corresponding OVGF results are compiled in Table 5. P3 IEs obtained with the cc-pVDZ basis are systematically lower than the 6-311G** results. Aug-cc-pVDZ results are dramatically better. Further expansion of the basis leads to systematic increases of IE predictions. The last entry in Table 4 presents the P3 IEs obtained in the cc-pVtrQZ basis. The cc-pVtrQZ IE values do not differ much from the cc-pVTZ IEs. In all bases, the same trends are obtained for the π_2−n_1 and π_3−n_2 pairs. The first pair is split by about 0.1 eV, whereas the second pair of levels is almost degenerate.

The OVGF results obtained in the cc-pVDZ basis are rather poor.[13] The IEs obtained with larger cc-type bases (Table 5) are much better and do not depend as much upon the basis as the P3 values. All of the lowest IEs are in fair agreement with experiment.[6,16]

The last column of Table 5 repeats the CASPT2 data of ref 25. The cc-pVtrQZ basis used in our calculations and the ANO/431/21 basis of ref 25 are approximately of the same quality. Whereas the CASPT2 IEs from the π-type orbitals are very close to the OVGF data, those of n-type levels are about 0.4−0.6 eV lower. Analogous trends are revealed in second-order electron propagator results (see Table 6). Here, energetic separations in the π_2−n_1 and π_3−n_2 pairs are 0.5−0.7 eV, with the n IEs being

TABLE 10: 9-Methyl Adenine ADC(3) IEs

	6-311G**		6-311++G**			
MO	KT	ADC(3)	KT	ADC(3)	UV PES[6]	TRPES[20]
π_1	8.24	8.03(0.88)	8.37	8.20(0.88)	8.39	~8.4
π_2	9.84	9.18(0.87)	9.98	9.33(0.87)	~9.4	~10.2
n_1	10.99	9.51(0.88)	11.13	9.69(0.88)	~9.4	~9.4
π_3	11.09	10.11(0.86)	11.21	10.26(0.86)	~10.2	
n_2	12.09	10.49(0.88)	11.22	10.66(0.87)	~10.2	~10.2
n_3	13.17	11.45(0.86)	13.30	11.62(0.86)	11.16	
π_4	13.40	12.07(0.69)	13.52	12.23(0.66)	11.93	
		12.61(0.16)		12.74(0.16)		
		13.19(0.01)		13.32(0.01)		
				13.93(0.02)		
π_5	14.53	13.19(0.68)	14.64	13.32(0.69)	12.81	
		12.61(0.08)		12.74(0.06)		

smaller. Second-order electron propagator results generally overestimate correlation corrections to KT results; these effects are especially pronounced for n levels. Similar trends appear in the CASPT2 study.

P3 results in Table 4 and OVGF results in Table 5 confirm published interpretations of spectra.[13,16] P3 calculations with correlation-consistent basis sets yield the same ordering as those of Tables 2 and 3 (π_1, n_1, π_2, n_2, π_3, n_3). Comparison of the OVGF data of Tables 5 and 2 discloses a remarkable stability with respect to changes in basis sets. Even the alteration of the ordering of the π_2-n_1 and π_3-n_2 pairs of states is maintained.

Adenine ADC(3) IEs. To give an alternative assessment of adenine IEs, the nondiagonal, renormalized ADC(3) method was applied. Four basis sets were used and the results are compiled in Table 7. PSs for each calculation are listed in parentheses. The one-electron nature of ionization is confirmed for the first six final states, for all of these PSs exceed 0.85. Significantly lower PSs correspond to the subsequent states. Shake-up final states with low PSs also are found in the ADC(3) calculations.

ADC(3) results confirm the OVGF order of final states as π_1, π_2, n_1, π_3, n_2, n_3. They predict that the second and third vertical IEs are within 0.15 eV of each other. A similar separation is obtained for the fourth and fifth vertical IEs. The energy difference between the first final state and the subsequent pair of final states is approximately 1 eV, as is the approximate separation between the π_2-n_1 and π_3-n_2 pairs. Another energy difference of about 1 eV also occurs between the latter pair of states and the n_3 final state. Except for the change in the order of the states that are responsible for the B and C bands of PES, the ADC(3) results confirm previous assignments.[13,16]

9-Methyl Adenine IEs. ***P3 and OVGF Results.*** Tables 8 and 9 present IEs of 9-methyl adenine obtained with the 6-311++G** and cc-pVtrQZ basis sets. There are only slight differences between results produced in these two basis sets. Compared with their counterparts in 9H-adenine, the IEs of 9-methyl adenine are shifted toward smaller values. The P3 results are closer than the OVGF data to the experimental values of ref 6. The gaps between the π_2 and n_1 levels and between the π_3 and n_2 levels become appreciable, especially with the OVGF method. The largest energy shifts are obtained for the π_2 (0.28 eV), π_3 (0.47 eV), and π_5 (0.42 eV) levels.

Lower π IEs for the methylated base may be understood in terms of the Dyson orbital plots of Figures 2 and 3. The greatest IE shifts correspond to π Dyson orbitals of adenine with the largest amplitudes at the 9 position. In the corresponding Dyson orbitals of the methylated compound, there is an antibonding relationship between π lobes on the C−H bonds of the methyl group and those that are on the nearest atoms of the adenine, five-member ring. This effect is called hyperconjugative by organic chemists, for it involves the saturated methyl group in the delocalization of π electrons. The π_1 and π_4 levels of 9-methyl adenine undergo smaller energy shifts, for their Dyson orbitals do not display this hyperconjugative feature.

ADC(3) Results. Table 10 shows ADC(3) IEs of 9-methyl adenine calculated with the 6-311G** and 6-311++G** basis sets together with the experimental data of refs 6 and 20. As was the case with adenine, the one-electron nature of ionization is confirmed for the first six ionization events. Relatively large energy gaps of 0.3−0.4 eV are predicted for the pairs of $\pi-n$ levels. The main line of the π_4 ionization is predicted at about 12.1−12.2 eV, which is in fair agreement with the experimental value of 11.93 eV. ADC(3) results confirm the ordering of final states obtained with P3 and OVGF calculation, π_1, π_2, n_1, π_3, n_2, n_3.[6]

Conclusions

Vertical ionization energies of 9H-adenine and its 9-methyl derivative were calculated with electron propagator methods and a variety of basis sets of increasing flexibility. The one-electron description of ionization holds for the first six levels, which correspond to three π and three n Dyson orbitals. A collapse of the one-electron picture of ionization is predicted for the higher-energy π_4 and π_5 levels. Energies of the first three cationic states were also assessed at the CCSD level of theory. Good agreement was achieved between ΔCCSD and electron propagator ionization energies. All calculations predict close energy proximity for the π_2-n_1 and π_3-n_2 pairs in 9H-adenine. These pairs are more separated in 9-methyl adenine. Methylation most affects the π_2, π_3, and π_5 levels through antibonding interactions between π lobes on two C−H bonds of the methyl group and the nearest π lobes of the adenine moiety.

Partial third order results on adenine give the following order of final states: π_1, n_1, π_2, n_2, π_3, n_3 and are in agreement with a recent assignment based on angle-resolved photoelectron spectra.[16] Outer valence Green's function and third-order algebraic diagrammatic construction predictions differ in the ordering of the π_2-n_1 and π_3-n_2 pairs of states. However, all computational methods agree that the π_2-n_1 and π_3-n_2 pairs of states are energetically close. The prediction of a small energy separation between the π_2 and n_1 final states contrasts with a recent assignment based on time-resolved photoelectron spectra in which the π_2 and n_2 cationic states were held to have similar energies.[20]

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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