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Reassignment of the low lying cationic states in gas phase adenine and 9-methyl adenine

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Abstract

Using time-resolved photoelectron spectroscopy results, we reassign the electronic character and ionization energies of the low lying cationic states of adenine and 9-methyl adenine. For adenine, the state ordering is $D_0(\pi^{-1}) = 8.5$ eV, $D_1(n^{-1}) = 9.6$ eV, $D_2(\pi^{-1}) \approx D_3(n^{-1}) \approx 10.5$ eV. For 9-methyl adenine, the assignment is the same with values of $D_0(\pi^{-1}) = 8.4$ eV, $D_1(n^{-1}) = 9.4$ eV, $D_2(\pi^{-1}) \approx D_3(n^{-1}) \approx 10.2$ eV.

1. Introduction

Knowledge of the electronic structure of a molecule is a prerequisite for understanding its dynamics. Adenine is of special interest since it is one of the nucleic bases [1]. In the gas phase, 9H-adenine (as illustrated in Fig. 1) is the energy-lowest tautomer and therefore the most abundant form [1,2]. A series of publications presented He(I) photoelectron spectra of various molecules, amongst them adenine and 9-methyl adenine [2–4]. For photon energies below 14 eV, the photoelectron spectra of adenine and 9-methyl adenine show six clearly separated bands, as in Fig. 1 and Table 1. The assignment of the electronic structure of the different cationic states, however, turned out to be rather difficult, especially for the lowest lying states. CNDO/2 calculations found that the first six cationic states were well separated in energy, leading to the assignment [3] of six cationic states corresponding to the six observed bands in the photoelectron spectrum (for adenine as well as for 9-methyl adenine, see Table 1). A more detailed study using HAM/3 and ab initio 4-31G SCF calculations, however, revealed that the cationic states $D_1(n^{-1})$ and $D_2(\pi^{-1})$ were very close in energy, as were the cationic

states $D_3(n^{-1})$ and $D_4(\pi^{-1})$. This led to the assignment of $D_1(n^{-1})$ and $D_2(\pi^{-1})$ to the second band and of $D_3(n^{-1})$ and $D_4(\pi^{-1})$ to the third band of the photoelectron spectrum [2,4]. This later assignment was supported by subsequent calculations [5–7]. Additional investigations employed various methods but concentrated on calculating only the lowest lying (vertical or adiabatic) ionization potential [8–10].

In this Letter we present results from time resolved photoelectron spectroscopy (TRPES) studies on adenine and 9-methyl adenine in the gas phase. The TRPES method and its applications have been recently reviewed [11,12]. TRPES can disentagle electronic from vibrational dynamics in excited molecules [13] by making use of the Koopmans' ionization correlations between excited states of the neutral molecule and those of the cation [14]. Here we make use of the known neutral excited states to assign those of the cation. Specifically, by making use of Koopmans' correlations, a reassignment of the low lying cationic states of adenine and 9-methyl adenine is proposed.

2. Experimental

Adenine (Sigma–Aldrich) and 9-methyl adenine (Fischer Scientific) were used without further purification. The experimental apparatus has been described in detail else-

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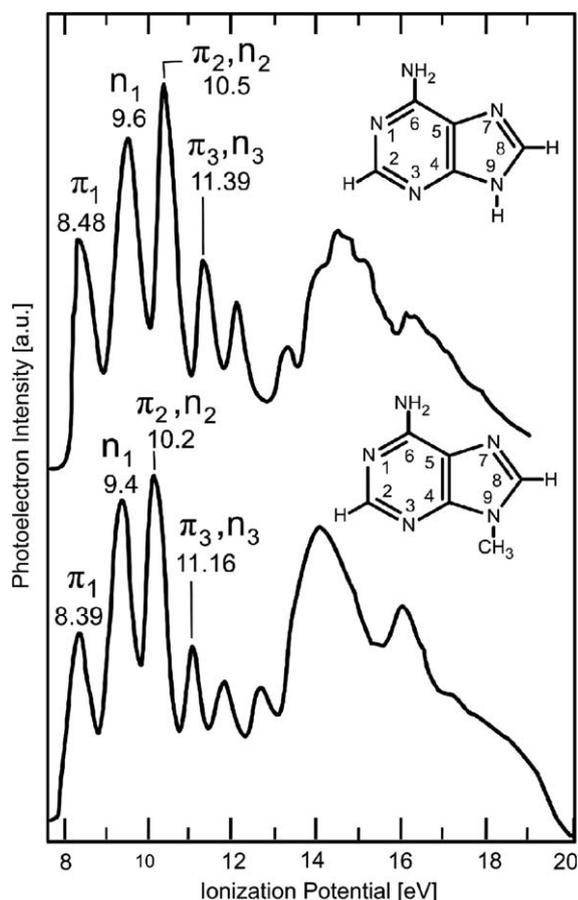*E-mail address:* albert.stolow@nrc.ca (A. Stolow).

Fig. 1. He(I) photoelectron spectra of adenine (top) and 9-methyl adenine (bottom), replotted from Ref. [2]. For the assignment of the ionization potentials, see the text and Table 1.

Table 1
Vertical ionization potentials (IP) in eV for 9-methyl adenine (top) and adenine (bottom)

Ion state	CNDO/2	HAM/3	IP
Ionization potentials for 9-methyl adenine			
$D_0(\pi^{-1})$	8.39	8.39	∼**8.4**
$D_1(n^{-1})$	9.42	9.42	∼**9.4**
$D_2(\pi^{-1})$	10.23	9.42	∼**10.2**
$D_3(n^{-1})$	11.16	10.23	∼**10.2**
$D_4(\pi^{-1})$	11.93	10.23	–*
Ionization potentials for adenine			
$D_0(\pi^{-1})$	8.48	8.48	∼**8.5**
$D_1(n^{-1})$	9.58	9.58	∼**9.6**
$D_2(\pi^{-1})$	10.50	9.58	∼**10.5**
$D_3(n^{-1})$	11.39	10.50	∼**10.5**
$D_4(\pi^{-1})$	12.10	10.50	–*

The CNDO/2 results are from Ref. [3], the HAM/3 from Ref. [2]. The –* means we cannot assign this cationic state from our TRPES data.

where [15,16]. The samples were brought into the gas-phase using a high temperature glass nozzle with an orifice of 500 μm diameter, heated to 180–230 °C. Pre-heated Argon at a stagnation pressure of 100–120 Torr was used as carrier gas. Recooling of the seed molecule was achieved via supersonic expansion. The absence of clusters was confirmed by mass spectrometry.

The laser system consists of a Ti:sapphire oscillator and 1 kHz regenerative amplifier, yielding about 2.7 mJ/pulse at a central wavelength of 800 nm. The pump (267 nm, ∼ 1 μJ) and probe (200 nm, ∼ 0.3 μJ) pulses were produced by generating the third and fourth harmonics of the 800 nm output, respectively. The two pulses were combined collinearly on a dichroic mirror and focussed mildly (f/80) into the interaction region using a spherical aluminum mirror. The pump-probe cross correlation (instrument response) of the experiment was ∼160 fs, measured by non-resonant, two-color multiphoton ionization of both NO and NH_3. Background signals due to single laser ionization were dynamically subtracted. Time-of-flight to energy calibration was obtained using photoelectron spectra from NO. Time constants and spectra were extracted from the 2D data using a Levenberg-Marquardt global fitting algorithm.

3. Results and discussion

The background subtracted time-resolved photoelectron spectra (converted to electron binding energy) for adenine and 9-methyl adenine are presented in Fig. 3a,c. The detailed analysis of the excited state electronic relaxation dynamics in adenine and 9-methyl adenine is reported elsewhere [17]. Here, we concentrate on the assignment of the cationic states. This assignment is based on the transient photoelectron spectra of the excited states that are involved in the relaxation dynamics. These spectra are extracted by a global fitting algorithm which models the 2D data according to

$$\mathrm{TRPES}(E_{\mathrm{kin}}, t) = \sum_{i=1,2} I_i(E_{\mathrm{kin}})[\exp(-t/\tau_i) \otimes g(t)],$$

where $I_i(E_{\mathrm{kin}})$ denotes the decay associated photoelectron spectrum having time constant τ_i and $g(t)$ is the cross correlation function (instrument response). The global fitting procedure yields values for the exponential time constants τ_i and determines the shape and amplitude of the decay associated photoelectron spectra $I_i(E_{\mathrm{kin}})$.

Two exponential time constants are needed to describe the TRPES signal of both 9-methyl adenine and adenine [17]. The fit yields $\tau_1 = 70$ fs (± 25 fs) and $\tau_2 = 1.1$ ps (± 0.11 ps) for 9-methyl adenine and $\tau_1 = 40$ fs (± 20 fs) and $\tau_2 = 1.2$ ps (± 0.18 ps) for adenine. The photophysical dynamics in 9-methyl adenine are well described by the following model [17]:

$$S_0 \xrightarrow{h\nu} S_2(\pi\pi^*) \xrightarrow{\tau_1} S_1(n\pi^*) \xrightarrow{\tau_2} S_0.$$
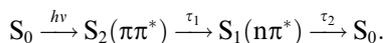
Upon absorption of a 267 nm photon, the molecule is excited into $S_2(\pi\pi^*)$. With the fast time constant ($\tau_1 = 70$ fs), the molecule electronically relaxes into $S_1(n\pi^*)$ and, from there, back to the S_0 ground state with the slower time constant ($\tau_2 = 1.1$ ps). Using TRPES, we can record, separately, the photoelectron spectra of $S_2(\pi\pi^*)$ and $S_1(n\pi^*)$. This is illustrated in Fig. 2. Excitation at 267 nm brings
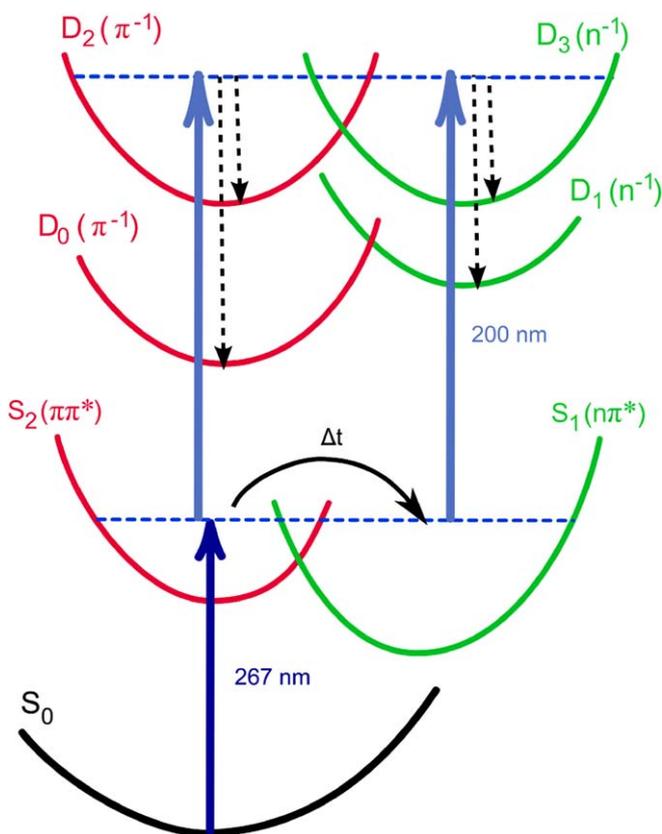
Fig. 2. Schematic description of the photoionization of 9-methyl adenine and adenine in the TRPES experiment. Koopmans' correlations allow for a mapping of different excited states onto different ionic states. The known character of the excited states permits assignment of the various photoelectron bands observed. The figure shows the assignment given in the text.

the molecule into the S_2 state, which has $\pi\pi^*$ character and, through Koopmans' correlations, ionizes into cationic π-hole states. For delay times >1 ps, the molecule has the $n\pi^*$ character of the S_1 state and photoionization is into the cationic n-hole states. Energy resolution allows the photoelectron spectra of S_2 and S_1 to be separated. In Fig. 4, we employ a simple Gaussian fit to the photoelectron bands in order to assist in the assignment.

Assignment of the cationic states D_0, D_1 and D_2 in 9-methyl adenine. Since the initially excited state has $\pi\pi^*$ character, from simple Koopmanns' correlations, ionization is allowed into cationic π-hole states. As can be seen in Fig. 3b, the photoelectron spectrum of the $\pi\pi^*$ state has two peaks at about 8.8 eV and ca. 10.5 eV. As suggested by the dashed lines in Fig. 4a, the spectrum can be represented by two Gaussians centered at 8.8 eV and 10.5 eV.

If $D_1(n^{-1}) \approx D_2(\pi^{-1}) \approx 9.4$ eV, as was previously suggested [2,4–6], then we would expect to see a contribution of $\pi\pi^* \rightarrow D_2(\pi^{-1})$ in the photoelectron spectrum at 9.4 eV. Since we have a gap in the $\pi\pi^*$ photoelectron spectrum in 9-methyl adenine, we conclude that there is no π-hole cationic state at 9.4 eV. Therefore, we have the following assignment of the three lowest lying cationic states of 9-methyl adenine: $D_0(\pi^{-1}) \approx 8.4$ eV, $D_1(n^{-1}) \approx 9.4$ eV and $D_2(\pi^{-1}) \approx 10.2$ eV. The Gaussians in Fig. 4a are centered at 8.8 and 10.5 eV. The values previously reported were 8.4 and 10.2 eV, respectively. This discrepancy is explained by the ~0.2 eV excess vibrational energy due to the 267 nm photon. (N. B. rigid molecules ionize into electronic states of the cation with similar vibrational energy as in the excited state [18]).
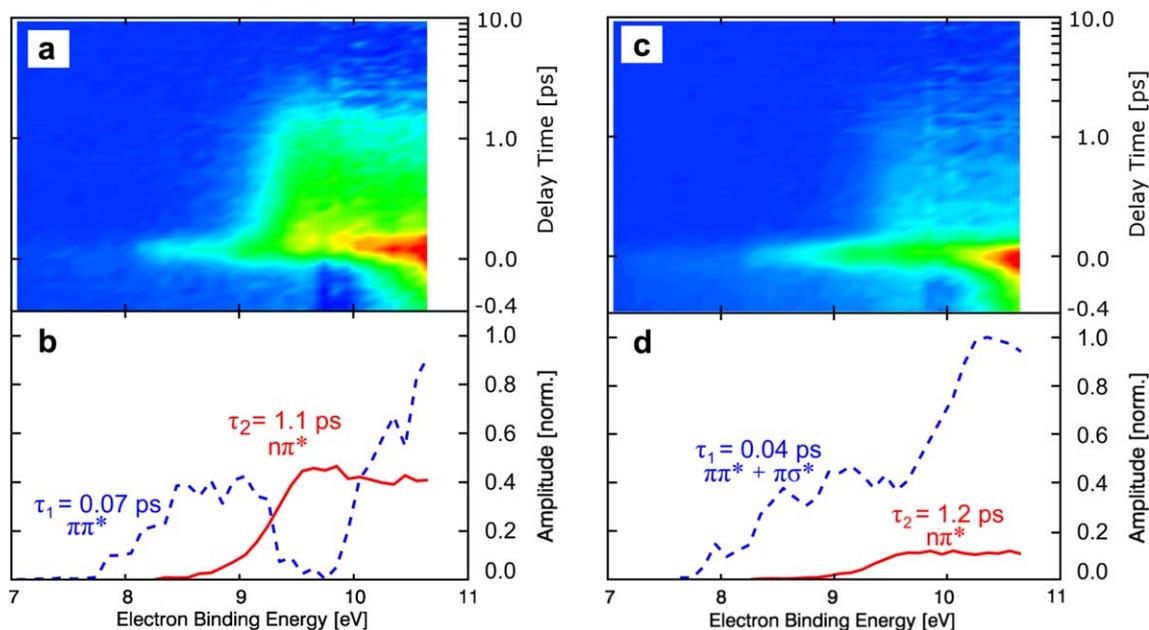

Fig. 3. Background subtracted TRPES data for 9-methyl adenine (a) and adenine (c). The time dependence is plotted on a linear/logarithmic scale with a linear scale in the region −0.4 to 1.0 ps and a logarithmic scale for delay times 1.0–10.0 ps. The lower panels (b) and (d) show the decomposition into photoelectron spectra of the relevant excited states, obtained from the global fitting algorithm (see the text).
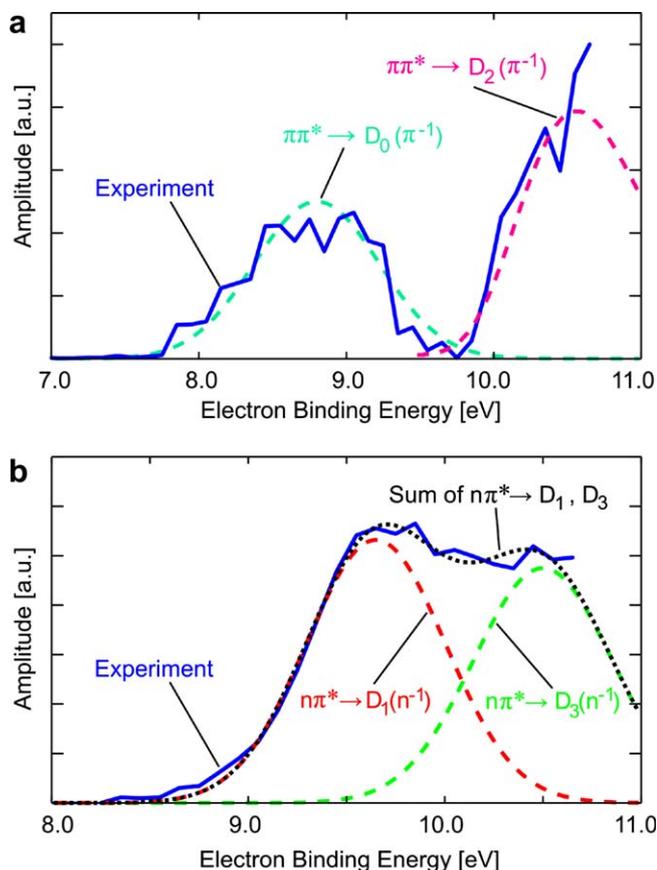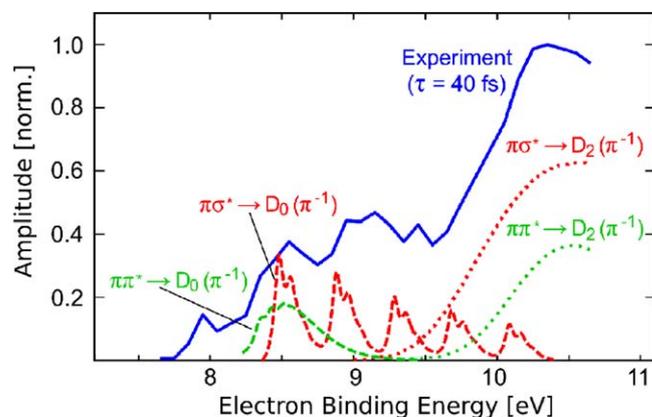
Fig. 5. Decay-associated spectrum of the fast time constant of adenine ($\tau = 40$ fs, solid line) and calculated Franck-Condon spectra for the transitions $\pi\pi^*/\pi\sigma^* \to D_0$ (dashed lines) and $\pi\pi^*/\pi\sigma^* \to D_2$ (dotted lines; Franck-Condon spectra replotted from Ref. [17]).

Fig. 4. Gaussian fits to the decay associated spectra of 9-methyl adenine from Fig. 3b. The assignments are as shown.

Assignment of the cationic state D_3 in 9-methyl adenine. The $n\pi^*$ photoelectron spectrum covers the electron binding energies >9 eV, as shown in Fig. 3b and Fig. 4b. This spectrum may be approximated using two Gaussians, centered at ~ 9.4 and ~ 10.2 eV, as illustrated by the dashed line in Fig. 4b. From Koopmanns' correlations, we expect that $n\pi^*$ ionizes into n-hole cationic states. Above we concluded that $D_1(n^{-1}) \approx 9.4$ eV. Since the $n\pi^*$ state photoelectron spectrum also covers the 10.2 eV energy region, we must conclude that there is another n-hole cationic state at ~ 10.2 eV. Our assignment therefore is $D_2(\pi^{-1}) \approx D_3(n^{-1}) \approx 10.2$ eV.

Assignment of the cationic states in adenine. The electronic relaxation dynamics in adenine are more complex and discussed in detail elsewhere [17]. Briefly, the photoelectron spectrum of the fast component ($\tau_1 = 40$ fs) has two contributions: $\pi\pi^* \to$ Ion and $\pi\sigma^* \to$ Ion. A major part of the excited state population in adenine takes the pathway $\pi\pi^* \xrightarrow{\tau_1^a} \pi\sigma^* \xrightarrow{\tau_1^b} S_0$. The rest of the population takes a pathway similar to 9-methyl adenine: $S_0 \xrightarrow{h\nu} S_2(\pi\pi^*) \xrightarrow{\tau_1^c} S_1(n\pi^*) \xrightarrow{\tau_2} S_0$. The TRPES experiment cannot distinguish between τ_1^a, τ_1^b and τ_1^c and the global fitting procedure can only extract a time constant for the combined process $\pi\pi^* \to \pi\sigma^*$, $\pi\sigma^* \to S_0$ and $\pi\pi^* \to n\pi^*$.

The $n\pi^*$ spectra of 9-methyl adenine (Fig. 3b) and adenine (Fig. 3d) are almost identical in shape. The $n\pi^*$ spec-

trum of adenine has a lower amplitude which reflects the fact that only a part of the population takes the pathway $\pi\pi^* \to n\pi^* \to S_0$. It is easy to verify that the $n\pi^*$ spectrum of adenine in Fig. 3d can be reconstructed in the same way as in the case of 9-methyl adenine in Fig. 4b. This leads us to the assignment of the cationic n-hole states at ≈ 9.6 and ≈ 10.5 eV.

For the assignment of the π-hole cationic states, it is straightforward to draw the analogous two Gaussians for the $\pi\pi^*/\pi\sigma^*$ photoelectron spectrum in Fig. 3d as was done for the $\pi\pi^*$ photoelectron spectrum of 9-methyl adenine in Fig. 4a. The peaks at 8.5 and 10.3 eV can be nicely reconstructed in this way. We therefore assign the cationic π-hole states in adenine to the He(I) photoelectron peaks at ≈ 8.5 and ≈ 10.5 eV. Could there be a π-hole state at ≈ 9.6 eV? If this were the case, we would expect to see a peak in the $\pi\pi^*$ photoelectron spectrum of adenine. This spectrum, however, has a peak around 9 eV, whereas at 9.6 eV there is a small dip. In Fig. 5 we re-plotted the Franck–Condon structures for $\pi\pi^* \to D_{0,2}$ and $\pi\sigma^* \to D_{0,2}$ that were calculated and discussed in Ref. [17]. The sum of these four spectra nicely reconstruct the spectrum of the fast ($\tau = 40$ fs) component. The $\pi\pi^*/\pi\sigma^*$ photoelectron spectrum is thereby reconstructed with $D_0(\pi^{-1}) \approx 8.5$ eV and $D_2(\pi^{-1}) \approx 10.5$ eV. No contribution from ionization into a cationic π-hole state at 9.6 eV is necessary. Moreover, the geometries and He(I) photoelectron spectra of adenine and 9-methyl adenine are quite similar [1,2]. We note that the (relative) assignment of the cationic states by LeBreton and co-workers was the same for 9-methyl adenine and adenine [2–4]. We therefore come to the following assignment of the cationic states of adenine: $D_0(\pi^{-1}) \approx 8.5$ eV, $D_1(n^{-1}) \approx 9.6$ eV, $D_2(\pi^{-1}) \approx D_3(n^{-1}) \approx 10.5$ eV. We cannot unambiguously assign the even higher lying cationic states since our time-resolved photoelectron experiment only covers the energy region up to 10.8 eV. Our assignments are summarized in Table 1.

In conclusion, time-resolved photoelectron spectroscopy was used to reassign the four lowest lying cationic states of

adenine and 9-methyl adenine. For adenine, the state ordering is $D_0(\pi^{-1}) = 8.5$ eV, $D_1(n^{-1}) = 9.6$ eV, $D_2(\pi^{-1}) \approx D_3(n^{-1}) \approx 10.5$ eV. For 9-methyl adenine, the ordering of the cationic states is the same with values of $D_0(\pi^{-1}) = 8.4$ eV, $D_1(n^{-1}) = 9.4$ eV, $D_2(\pi^{-1}) \approx D_3(n^{-1}) \approx 10.2$ eV.

Note added in proof

A very recent paper by Roca-Sanjuán et al. (Journal of Chemical Physics 125, 084302, 2006) presents high level ab initio results for the calculation of ionization potentials and cationic state ordering in isolated DNA bases. For adenine, they calculate the same state ordering as presented here.

Acknowledgements

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