Acta Physica Universitatis Comenianae
Vol. L–LI, Number 1&2 (2009–2010) 67–76

A Comprehensive Study of Fragmentation of the DNA Base Adenine Induced by Low Energy Electron Attachment*

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Abstract: Dissociative electron attachment (DEA) to the DNA base adenine became of a considerable interest since the discovery that low energy electrons can effectively damage DNA below the ionization threshold. In order to understand the mechanisms of damaging the complex DNA structure, the knowledge about the dissociative electron attachment process to DNA building blocks has to be collected. Here we present a detailed study of the dissociative electron attachment to adenine with special emphasis upon the various fragmentation pathways. The dominant low energy resonances at about 1 eV are investigated by means of partially deuterated and methylated adenine compounds. Insight into the fragmentation process for DEA at higher electron energies is obtained by embedding adenine molecules into cold helium droplets.

1. Introduction

The interaction of low energy electrons with gas phase molecules is a fundamental process in technical and natural plasmas and has been studied for a large number of molecules [1]. In the very low energy range (below the ionization threshold) electrons can attach to molecules and form negatively charged species besides other inelastic and elastic scattering channels. Energy and momentum conservation, however, do not enable the formation of stable anions of the formerly neutral target molecules. As schematically shown in Figure 1, the attachment of a free electron to a molecule AB initially forms an unstable transient negative ion (TNI) state, AB^{-*}, with the same geometry as the neutral precursor (vertical Franck Condon transition). Often the attached electron occupies an antibonding orbital or the vertical transition ends up at the repulsive part of a (binding) potential energy curve that starts to separate parts of the transient negative ion. Such an immediate decay of TNI resonances (localized on DNA basic constituents) was also assumed to be responsible for formation of strand breaks in plasmid DNA when irradiated with electrons below the ionization threshold [2]. In order to deepen the understanding of these processes numerous studies have been dedicated to the investigation of free dissociative electron attachment (DEA) to isolated biomolecules in the gas phase in recent years (see reviews [3, 4]).

**)* *We would like to dedicate this paper to our friend and colleague Professor Peter Lukáč on the occasion of his 70th birthday. We are grateful for his long lasting and successful efforts concerning a very fruitful collaboration between our two institutes leading to more than 120 joint publications and the graduating of 10 joint PhD students. This great achievement has been recently officially recognized by the Universität Innsbruck by awarding to Peter Lukac the Ehrenbürgerschaft in 2008.*

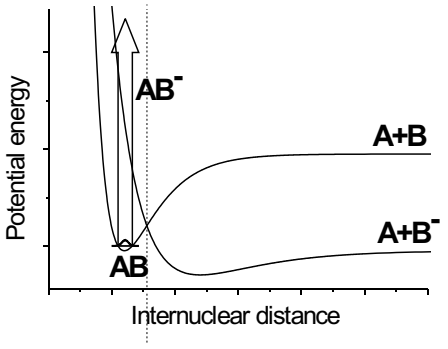

Fig. 1. Schematic potential energy diagram of a neutral molecule AB and the anion AB^-. DEA to the neutral molecule leads to a vertical transition (indicated by the arrow) to the repulsive part of the anionic potential energy curve. Autodetachment is possible until A and B^- are separated beyond the vertical dashed line where the two potential energy curves cross each other.

An experimental approach to reveal the mechanism of DNA damage is to start with studies of the building blocks of DNA and then to proceed to more complex biological systems. So far the most studied isolated DNA compounds have been the nucleobases [5–7]. We extended our studies also to the sugar deoxyribose [8] and sugar analogues [9] and only recently the group of Eugen Illenberger carried out studies with ribose [10] and phosphate analogues [11]. For nucleobases the most abundant anion formed is the dehydrogenated molecular anion $(M–H)^-$ via reaction

$$e^- + M \quad M^{-*} \quad (M–H)^- + H \qquad (1)$$

For all nucleobases, process (1) is mainly operative at electron energies below 3 eV leading to a cross section structure with a few narrow peaks followed by broad resonances [5–7]. As several isomers for $(M–H)^-$ can be formed, further DEA experiments with partially deuterated thymine [6, 12–14] showed that reaction (1) leads exclusively to the loss of a hydrogen atom from the nitrogen sites. Further measurements with partially methylated pyrimidine nucleobases [12–14] finally revealed the exact site of the DEA process, i.e. all narrow vibrational progressions in the attachment cross section of $(M–H)^-$ result from the hydrogen loss from the N1 site while the broad resonance observed at about 1.8 eV was ascribed to the hydrogen loss from the N3 site. Thus, these previous experiments with the pyrimidines thymine and uracil demonstrated remarkable bond and site selectivity for the formation of $(M–H)^-$. Also for H^- formation, which is the complementary reaction channel of $(M–H)^-$ a similar site selectivity has been observed in DEA to the pyrimidines [15] and also simple organic molecules (see Ref. e.g., [16]). The relevance of these studies towards DNA damage increases due to the fact that some sites in a DNA complex are blocked for H-loss (e.g. the hydrogen at N1 site of thymine is not present in the base-sugar complex). In spite of the focus on the dehydrogenated anion we note that pyrimidines fragment extensively at higher electron energies [17] which we will show below to happen also for the purine nucleobase adenine.

Recently we also embedded nucleobases in cold helium droplets. The latter provides the ultimate low-temperature matrix for atoms and molecules [18]. Evaporative cooling produces an isothermal low temperature environment at 0.37 K in these droplets. This

temperature is lower than possible for most solid matrices. The droplets can be doped with atoms or molecules that can then interact to form completely novel molecular complexes either in the interior or at the surface of the droplet [18]. This has been demonstrated with spectroscopic studies for clusters doped with several molecules and molecular complexes including the Watson-Crick nucleobase pairs [19]. Electron impact ionization studies of (doped) He clusters are rather scarce [20] and the more such electron capture studies leading to anion formation in doped helium droplets [21].

So far the results observed for pyrimidines demonstrated the possibility to induce selectively chemical reactions by the attachment of electrons with specific energy. It is interesting to note that in electron induced chemistry such control has been also achieved utilizing inelastic tunneling of electrons in scanning tunneling microscopes [22]. Here we present the results for DEA to the nucleobase adenine isolated in the gas phase [23, 24] and embedded in helium droplets [25] (see Figure 2 for the schematic molecular structure). A dramatic change of the fragmentation pattern can be observed when going from isolated conditions to clusters in helium droplets. This allows conclusion concerning the fragmentation pathways of adenine upon DEA.

2. Experimental setup

For the present DEA experiments, three different setups are utilized, (i) a crossed electron/neutral beam apparatus consisting of a neutral molecular beam source, an electron monochromator and a quadrupole mass spectrometer (for more details see [5]), (ii) a double focusing mass spectrometer (VG-ZAB) [24] with attached oven and Nier type ion source and (iii) a double focusing mass spectrometer Varian MAT CH5-DF with the Nier type ion source and attached helium droplet source with pick-up chamber [21]. In all three setups a commercial adenine sample from Sigma Aldrich is used which has a stated purity of 99 %. Typical oven temperatures used in the present experiment are 453 K for setup (i), and about 400 K for setup (ii) and (iii), respectively. Thermal decomposition of the adenine powder does not play any role at these temperatures.

In the monochromator setup evaporated molecules effuse through a capillary with a diameter of 1 mm and a length of 8 cm directly into the collision chamber, where they interact with a monochromatized electron beam. The electrons are produced by a hairpin filament and are accelerated with a lens system into a hemispherical electrostatic field analyzer. After the hemispheres, the energy selected electrons are accelerated with a second lens system to the desired energy and are focused into the collision chamber crossing the neutral beam at a right angle. The monochromator measurements are performed with the electron energy resolutions between 75 and 120 meV. The reduced resolution of 120 meV is used to allow a higher detection sensitivity of the apparatus. The anions formed are extracted by a weak field into direction of the quadrupole mass spectrometer. The mass analyzed ion current is amplified by a channel electron multiplier operated in the pulse counting mode and detected using a computer.

Further measurements with adenine in the gas phase are carried out with a double focusing two sector field mass spectrometer (VG-ZAB) of reversed Nier–Johnson type BE geometry which provides a much higher sensitivity than the monochromator setup (see [24]). The oven is connected to the collision chamber of a Nier-type ion source via a

heatable capillary. The interaction of the neutral effusive molecular beam and the electron beam takes place in the collision chamber. The entire ion source is heated to about 390 K to avoid contamination of the surfaces. The electron current used is about 10 A at an electron energy resolution (FWHM) of about 1 eV. The ions formed in the ion source are extracted by a weak electric field and accelerated through a potential drop of 5 kV into the mass spectrometer. The mass analyzed ions are finally detected with a channel electron multiplier. For the present study with partially opened slits a mass resolution of about 2000 (m/ m, 10 % valley) is achieved.

The measurements with adenine embedded in helium droplets are performed with a He cluster source, a pick-up cell containing the vapor of the biomolecules and a Varian MAT CH5-DF two sector-field mass spectrometer [25]. The helium droplet beam is formed by expansion of helium gas into vacuum through a nozzle with an orifice of 5 μm at a stagnation temperature of 9.5 K and stagnation pressures of 10–15 bar. The mean size of the helium droplets is estimated to be a few 10^4. Then they are doped with adenine molecules in a differentially pumped region; the biomolecules originate from a resistively heated oven filled with the corresponding powder. The present experiments are performed with an electron energy resolution of about 1 eV and an electron current of 10 μA.

It is possible for all setups to record the ion current for mass selected anions as a function of the electron energy and, moreover, also the mass spectra at fixed electron energies. The energy scale is calibrated by measuring the ion yield of a calibration gas under same conditions. We use the electron attachment reaction SF_6 e SF_6 for calibration. The ion yield of this anion exhibits a peak at zero eV resulting from s-wave attachment to the neutral molecules and the width of the peak is a measure of the electron energy distribution.

3. Results and discussion

Figure 2 shows the negative ion mass spectra [24] of adenine at electron energies of approximately 2 eV and 6 eV recorded with the VG-ZAB apparatus introduced above. These electron energies are close to the energies of the two main resonances observed in the DEA cross sections of adenine. The comparison of these mass spectra reveals a characteristic difference in fragmentation, i.e. there is substantially less fragmentation by ring cleavage in the mass spectrum recorded at 2 eV. The latter spectrum is dominated by the dehydrogenated $(A\text{-}H)^-$ anion (mass 134 u) with its isotopomers which is formed via reaction (1). The second strongest ion present in the mass spectrum produced via

$$e + A \quad A^{-*} \quad CN^- + \text{neutral fragments} \qquad (2)$$

is CN^- (mass 26 u with an isotopomer at 27 u) which has an intensity of about 10 % of the $(A\text{-}H)^-$. A weak signal (about 0.3% of the main peak) is observed at 118 u. We assign this anion as $(A\text{-}NH_3)^-$ that is formed via loss of an NH_3 group from the TNI A^{-*}. Similarly, we tentatively assign the masses 116 u, 117 u, 119 u and 120 u to the ions formed via loss of $NH_3 + H_2$, $NH_3 + H$, NH_2 and NH from adenine. The (small) peak at mass 85 u is an artifact as it is present also in the background mass spectrum, i.e. when the adenine sample in the oven is not heated.

The lower panel of Fig. 2 shows the negative ion mass spectrum of adenine recorded at 6 eV. In contrast to the 2 eV spectrum a large number of fragment ions can be observed.

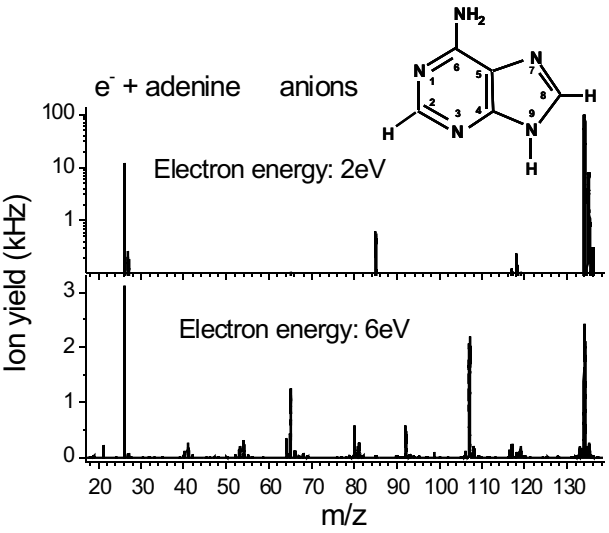

Fig. 2. Negative ion mass spectra of adenine measured at the electron energy of 2 eV and 6 eV utilizing the sector field mass spectrometer VG-ZAB [24]. The electron current and the oven temperature are set to 10 μA and 453 K, respectively. A schematic view of the molecular structure of adenine is also included in the figure.

The dominant anion at this energy is the CN^- (26 u). Even at 6 eV electron energy the dehydrogenated ion $(A\text{-}H)^-$ is still present as the second strongest anion. Nearly the same abundance has the ion with mass 107 u which is most probably formed via loss of neutral H and HCN from adenine. Abdoul-Carime et al. [26] reported in their DEA study to adenine the formation of an anion with a mass of 108 u which was assigned to the loss of an HCN group. An ion with a mass of 108 u can also be identified in the present mass spectrum, however, its intensity is one order of magnitude less than that of the ion at 107 u. In contrast to the 2 eV mass spectrum, several additional fragment ions are present in the 6 eV spectrum. The ion having a mass of 92 u is formed most likely via loss of CN and NH_3 from adenine. We tentatively assign the mass at 65 u to the dicyanomethyl negative ion $HC(CN)_2$ and the mass 64 u may be associated with the C_3N_2 anion. Additional negative fragment ions are also detected at 54 u, 53 u, 41 u and 40 u.

After determination of the most abundant anions in the mass spectra, ion yields as a function of the electron energy have been measured for these anions. Figure 3 shows the ion yield of $(A\text{–}H)^-$ measured with an electron energy resolution of about 75 meV. The ion yield shows narrow peaks at 0.79 eV, 0.91 eV and 1.15 eV, followed by two broader features at about 1.4 eV and 2.2 eV. Such ion yield consisting of a combination of narrow peaks and broad resonances is similar to the dehydrogenated anion yield of pyrimidines [14]. The resonance formation was discussed extensively in [14] for the thymine case where the sharp peak structure was ascribed to vibrational Feshbach resonances which decay by tunneling of the N1-hydrogen atom through a potential barrier formed due to an avoided crossing between the potential curves of the lowest state and a dipole bound state formed after electron capture [14]. The broad resonances in the anion yield were ex-

plained in terms of a predissociation process of a resonance identified in electron transmission spectroscopy [27] by higher lying resonances [28].

Due to five possible isomeric structures of $(A-H)^-$ the other intriguing question in formation of this anion concerns the site of hydrogen loss. By quantum chemical methods the threshold of anion formation for each $(M-H)^-$ isomer can be determined by calculating the BDE-EA energy (BDE = bond dissociation energy, EA = electron affinity). Using the values presented in [23], we obtain 3.63 eV, 1.72 eV, 2.53 eV and 0.94 eV for H loss from C2, N6, C8 and N9, respectively. In detail, the BDE values presented in [23] (calculated with the G2(MP2) extrapolation method with an estimated accuracy of 0.2 eV are 4.74 eV, 4.69 eV, 5.06 eV and 4.38 eV for hydrogen release from C2, N6, C8 and N9 respectively. The electron affinities (EAs) for the different (M–H) isomers are 1.11 eV, 2.97 eV, 2.53 eV and 3.44 eV with hydrogen released from C2, N6, C8 and N9. These values are in good to fair agreement with previous calculations of other groups [29, 30]. Therefore, according to the calculations, the narrow peaks below 1.72 eV can be assigned to hydrogen loss from the N9 position. The validity of the calculations can be checked experimentally by measurements with 9-methyladenine (9-mAd) where the hydrogen at N9 position is replaced by a methyl group [23]. The corresponding measured ion yield of $(M-H)^-$ for 9-mAd is shown in Fig. 3. Except for a minor peak close to zero eV which is possibly formed via ion molecule reactions of adenine with SF_6 / SF_6 or ion formation from DEA to vibrationally excited neutral adenine molecules (formed by the heating process), no ion yield is observed below 1.6 eV. The conclusion is that all the resonances below this energy are formed by hydrogen loss from the N9 position. This is in contrast to electron energies above 1.6 eV (i.e. the 2 eV peak shown in the middlepanel of Fig. 3), where H-loss from other positions may be responsible.

In order to obtain additional information on the fragmentation site for energies above 1.6 eV, we performed two further studies with adenine derivates labeled at other position [23]. For example, we measured the $(A-H)^-$ spectrum for C2-deuterated adenine (2-d-Ad) investigating, if hydrogen loss from the C2 site occurs. The ion yield for 2-d-Ad shown in Fig. 3 is almost identical to $(A-H)^-$ from Ad with no $(M-D)^-$ anions observed at all. The lesser resolved first three peaks can be ascribed to the slightly worse energy resolution used for this measurement. Thus, H-loss from the C2 site can be ruled out to occur in the DEA process leading to $(M-H)^-$. Also measurements with partially methylated adenine (6-dimAd), where hydrogen release from the amino group at C6 is blocked by two methyl groups, show no disappearance of $(M-H)^-$ ion signal above 1.6 eV [23]. Moreover, hydrogen loss from C8 cannot be responsible for the peak at 2 eV as the calculated threshold energy for $(M-H)^-$ with H-loss from C8 with 2.53 eV is much higher than the position of the resonance under question. Therefore, hydrogen loss from another position than C2, C8 and the amino group at C6 must be also responsible for the occurrence of the 2 eV peak (see middlepanel of Fig. 3). It seems that there is still a substantial contribution to the ion yield from N9 position (see detailed discussion in [23]).

Thus, the overriding conclusion with respect to site selective hydrogen loss is that the hydrogen loss occurs almost exclusively from the N9 position. It was also found additionally [23] that the shape of the spectra is strongly influenced by the functional groups at C6, i.e., going from C6-H to C6-NH_2, and to C6-$N(CH_3)_2$. For all the results in this context and a detailed discussion of this effect by means of quantum chemical calculations we refer to our communication [23]. In short, the compounds differ by a considerably different elec-

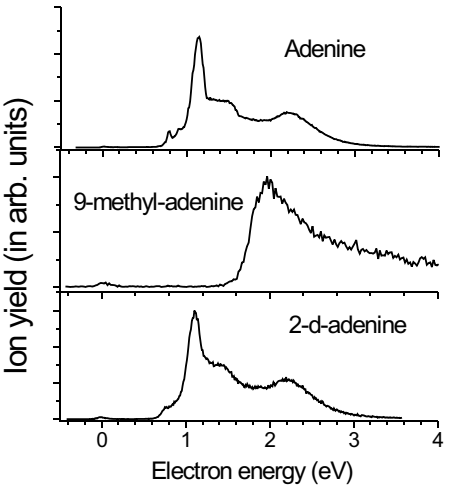

Fig. 3. Ion yield for the dehydrogenated parent anion formed upon DEA to adenine, 9-methyladenine, and C2 deuterated adenine (2-d-Ad), measured with the high resolution electron monochromator [23].

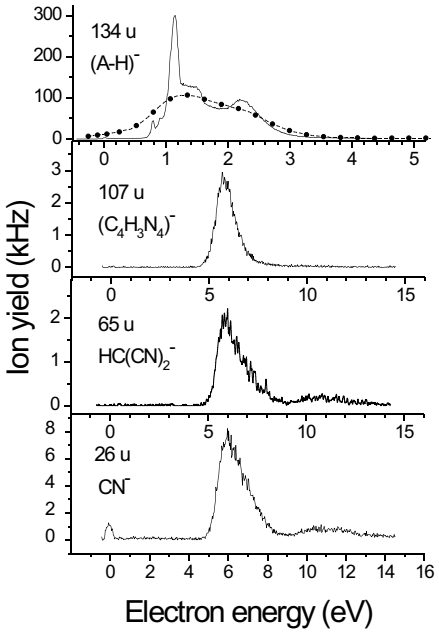

Fig. 4. Ion efficiency curves for the ions with masses 134 u, 107 u, 65 u and 26 u formed via DEA to adenine. The solid lines represent measurements utilizing the high-resolution electron monochromator [23] normalized to the anion efficiency curves measured with the sector field mass spectrometer VG-ZAB [24]. The ion yield of the dehydrogenated parent anion measured with this sector field instrument is also included in top panel (dashed line with full circles).

trical field situation at the N9-H bond by means of a changing dipole moment. Also the lowest virtual * MOs of the neutral derivatives show distinct differences in the wave function density close to C6 [23].

We show in Fig. 4 the ion efficiency curves for the $C_4H_3N_4$ (107 u), $HC(CN)_2^-$(65 u) and CN^- (26 u) anions which are upon the most abundant anions formed at 6 eV (see Fig. 2). All three anions (like many other fragment anions of adenine not shown here [24]) are formed in a main resonance at about 5.8 eV, i.e. these anions derive from the same temporary negative ion state. The ion at 107 u is most likely formed via the loss of HCN and an additional H atom. This reaction is energetically more favorable than the formation of a CN radical and an H_2 molecule. Also the CN^- anion belongs to the principal ions formed via DEA to adenine. It is formed via a complex fragmentation mechanism and is in the energy range above 5 eV the most intense anion (see mass spectrum in Fig. 2). It turned out in the course of the investigations that the low energy contribution close to zero eV is strongly (ion source) temperature dependent. This observation means that adenine molecules hitting a hot wall of the ion source may thermally decompose and therefore contribute to an increase of the anion efficiency curves of this specific fragment at low electron energies.

To gain more insight in the fragmentation processes upon DEA, we also embedded adenine in cold helium droplets and studied the DEA processes at a temperature of 0.37 K. The corresponding measurement of $(A\text{-}H)^-$ in the helium droplets is shown in Fig. 5. The electron energy scale of the ion yield measured in the droplets is shifted by 1.1 eV downwards. This energy is required for the electrons to penetrate into the He droplets [20, 21]. Taking into account this shift allows a direct comparison with the gas phase data which are also included in the figure. All the data presented in the graph are shown with the same energy resolution of ~1 eV (see Fig. 4 showing the effect of energy resolution by the comparison of high- and low-resolution data for $(A\text{-}H)^-$). Also when adenine is embedded in helium droplets the low energy resonance at about 1.2 eV is formed. However, in striking contrast to the gas phase case in helium droplets $(A\text{-}H)^-$ production is observed at electron energies as high as 15 eV with a higher abundance than the low energy feature. Other fragment anions, including the hydride anion formed abundantly in the gas phase, are in case of DEA to adenine in helium droplets below the detection limit of the apparatus. This leads to the conclusion that dissociation by ring cleavage is suppressed by the presence in the cold helium environment which acts as a sink for the internal excess energy of the formed anion intermediate $(A\text{-}H)^{-*}$. We suspect that this is due to energy relaxation prior to dissociation. This interpretation is supported by the shape of the sum of all anions (total ion yield) for the fragment anions formed in the case of gas phase target (also included in Fig. 5). The remaining question is: why the ratio of the low and high energy resonance differs so strongly between gas phase and helium droplets? The answer can be found most likely in effects like the injection behavior of the electron beam into the droplet near threshold and the different autodetachment behavior of the low energy resonance between a bare gas phase molecule and one solvated in the helium [31]. A minor contribution may originate from the different intensity profile of the electron beam in the two setups in the very low energy region [31]. Such a reversal in relative abundance was already observed also for the formation of the dehydrogenated closed-shell anion of thymine [21, 25] and the parent anion of TNT^- [31]. Similar to the present case also for TNT no fragmentation in the helium droplet was observed at all.

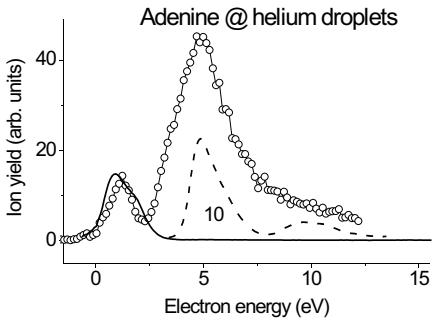

Fig. 5. Ion yield of the dehydrogenated parent anion $(A\text{-}H)^-$ of adenine measured in helium droplets (solid lines with open circles) [25], $(A\text{-}H)^-$ formed upon DEA in the gas phase (solid line) and sum of all other product anions observed upon DEA to the corresponding bare molecules (dashed line) [24]. The electron energy scale of the symbol graph is shifted downwards by 1.1 eV to account for the energy required for the electrons to penetrate the droplet. For better clarity the total ion yield above 3 eV is multiplied with a factor of ten (see text).

4. Conclusion

In conclusion, we performed a detailed study of the dissociative electron attachment to adenine under isolated conditions and in a cold helium droplet matrix. DEA to the isolated molecules leads to strong fragmentation at higher electron energies while the dehydrogenated parent anion dominates at low energies. The anion yield of $(A\text{-}H)^-$ below 1.6 eV can be ascribed to the hydrogen loss from the N9 position while, above this energy, a rather minor contribution is also formed by the H-loss from another site. We observe a strong dependence of the peak structure on the presence of different functional groups at the C6 site. Quantum chemical calculations show a strong modification of the electrostatic potential leading to a change in the dipole moment and, thus, influencing the structure of DEA spectra.

Embedding adenine in helium droplets shows strongly modified spectra as the helium droplet acts as a sink for the internal excess energy of the formed anion intermediate $(A\text{-}H)^{-*}$. This prevents subsequent fragmentation of this anion into smaller negatively charged and neutral fragments which is an efficient reaction channel for the gas phase situation. In view of radiation damage of complex DNA systems by secondary electrons, the present results indicate that the simple H loss leading to the exclusive formation of $(A\text{-}H)^-$ anions prevails over the further dissociation of this anion and, moreover, over extensive hydride loss. This is in contrast to preferential H^- desorption from electron irradiated films of thymine and plasmid DNA [2, 4].

Acknowledgments

This work was supported in part by the FWF, Wien, and the European Commission through the networks ITS-LEIF, COST-P9, EIPAM and RADAM. S.D. gratefully acknowledges an APART grant from the Austrian Academy of Sciences.

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