

Direct Damage of Deoxyadenosine Monophosphate by Low Energy Electrons Probed by X-Ray Photoelectron Spectroscopy

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Supporting Information

XPS Peak Analysis

The envelope of each elemental transition in the XPS spectrum can be de-convoluted into component peaks which represent distinct bonding environments of the element in the molecule. This is done by the CASAXPS software, where peak shapes were set as a product of Gaussian and Lorentzian functions, with 90% and 10% weighting, respectively. The spectrum baseline was fit with a Shirley background and subtracted from the peak areas. The minimum number of components which represent the distinct chemical environments of an element and minimizes the residual error, are used to fit the envelopes. All spectra of a given element are subjected to the

same fitting constraints. The assignment of components for all elements were done according to references to previous studies.

Figure S1 shows the O-1s and N-1s photoelectron spectra before ((a) and (c)) and after ((b) and (d)) irradiation with electrons of energies 3, 5, 10 and 25 eV. Irradiation at all energies were repeated 3 times on fresh samples and the plots are averaged over the 3 data sets. Due to the drastic fall in electron flux at energies below 10 eV, the duration of irradiation required to see observable changes in the photoelectron spectra ranged from 2 hours at 25 eV to almost 24 hours at 3 eV. The interesting thing to note is that the irradiated photoelectron spectra for both transitions look similar for all four energies and also for other energies between 3 and 25 eV which are not shown here.

The components are labelled with the suffixes i, ii,... with increasing binding energy. Oⁱ represents the O atoms in the phosphate group, i.e. P=O, P-O⁻ and P-OH. Since our samples are prepared under atmospheric conditions, we expect the presence of adventitious hydrocarbons and water on our sample, due to which O in the carbonyl group (C=O) can contribute to Oⁱ. Oⁱⁱ is assigned to O atoms in the sugar (C-O-C, C-O-H) and in the phosphoester bond (C-O-P) and has some contribution from oxygen containing adventitious species, while Oⁱⁱⁱ is due to water. It is to be noted that the O-1s photoelectron spectrum from pristine dAMP should have almost equal contributions from Oⁱ and Oⁱⁱ. Due to the presence of O-containing adventitious species, the actual spectra from our samples show a larger contribution from Oⁱⁱ, with the ratio of Oⁱ to Oⁱⁱ varying in range from 0.45 to 0.8. The N-1s spectral envelope is the result of N in two different bonding sites in the nucleobase: imine bonded nitrogen (-N=) contributing to Nⁱ and amine bonded nitrogen (NH₂, R₃N) contributing to Nⁱⁱ. The Nⁱ:Nⁱⁱ ratio from almost all dAMP samples closely follows the expected stoichiometric ratio of 60:40, as the N signal arises purely from the nucleotide molecules. The C-1s signal is best fit with three peaks. Cⁱ at the lowest energy is the largest peak which arises

from carbon atoms in C–C and C–H bonds, both from the analyte and adventitious hydrocarbons. Cⁱⁱ is assigned to carbon atoms in C–O, C–N, and N–C–N bonds, as well as C–O–C bonds on residual hydrocarbons. Cⁱⁱⁱ is assigned to carbon atoms in N=C–N and C–NH₂ bonds and possibly also the carbon in the glycosidic N–C–O bond. According to some references, and also our earlier work in which nucleotide spectra were obtained at a higher resolution than the current work, a fourth peak could be fit at the highest energy, which was assigned to the glycosidic carbon. It is likely that due to lower resolution of the present experiments, the C–1s envelope can only be resolved into three peaks. Again, the relative ratios of the C–1s components don't follow stoichiometry due to contribution from C-containing adventitious species, mainly to Cⁱ.

Upon electron irradiation, the general trend is an increase in Oⁱ and decrease in Oⁱⁱ with irradiation, which signifies breakage of C–O bonds and simultaneous formation of a new bond between P and O. One possibility is cleavage between C and O in the C–O–P phosphoester linkage which would lead to a loss in Oⁱⁱ intensity and a corresponding gain in Oⁱ since the O atom becomes part of the phosphate moiety in the process. Alternatively, the rise in Oⁱⁱ could indicate the formation of a carbonyl bond (C=O), since its signature overlaps with those from phosphate. The magnitude of Oⁱⁱⁱ remains almost constant showing that adventitious water is not affected by low energy electrons. It is to be noted that the contribution of Oⁱⁱⁱ varies between 2 to 5% of the total O1s envelope intensity for all the samples we studied which translates to a concentration of 1 water molecule per 20 or more nucleotide molecules. Therefore, it can be assumed that water likely does not play a significant role in the chemistry following electron irradiation, unlike some previous studies.

The evolution of the C–1s components with irradiation reveal further information about damage to the nucleotides. The cleavage between C and O in the C–O–P linkage, as concluded from the

O-1s signal, would result in the signal from C remaining in Cⁱⁱ or possibly shifting to the Cⁱ component. If there is formation of a new C=O bond, it will contribute to a rise in the Cⁱⁱⁱ signal. Instead, we see that Cⁱⁱⁱ goes down in intensity upon irradiation, thus ruling out the possibility of C=O formation and suggesting phosphoester bond breakage as the cause of Oⁱ growth. Cⁱⁱ also decreases in intensity, while Cⁱ increases with irradiation. The reduction in Cⁱⁱ and Cⁱⁱⁱ indicates breaking of some or all of the C–O, C–N, N–C–N, N=C–N and C–NH₂ bonds within the sugar and nucleobase ring structures and also the glycosidic N–C–O bond. The simultaneous increase in Cⁱ is expected since the resulting free C atoms would form new C–C and C–H bonds.

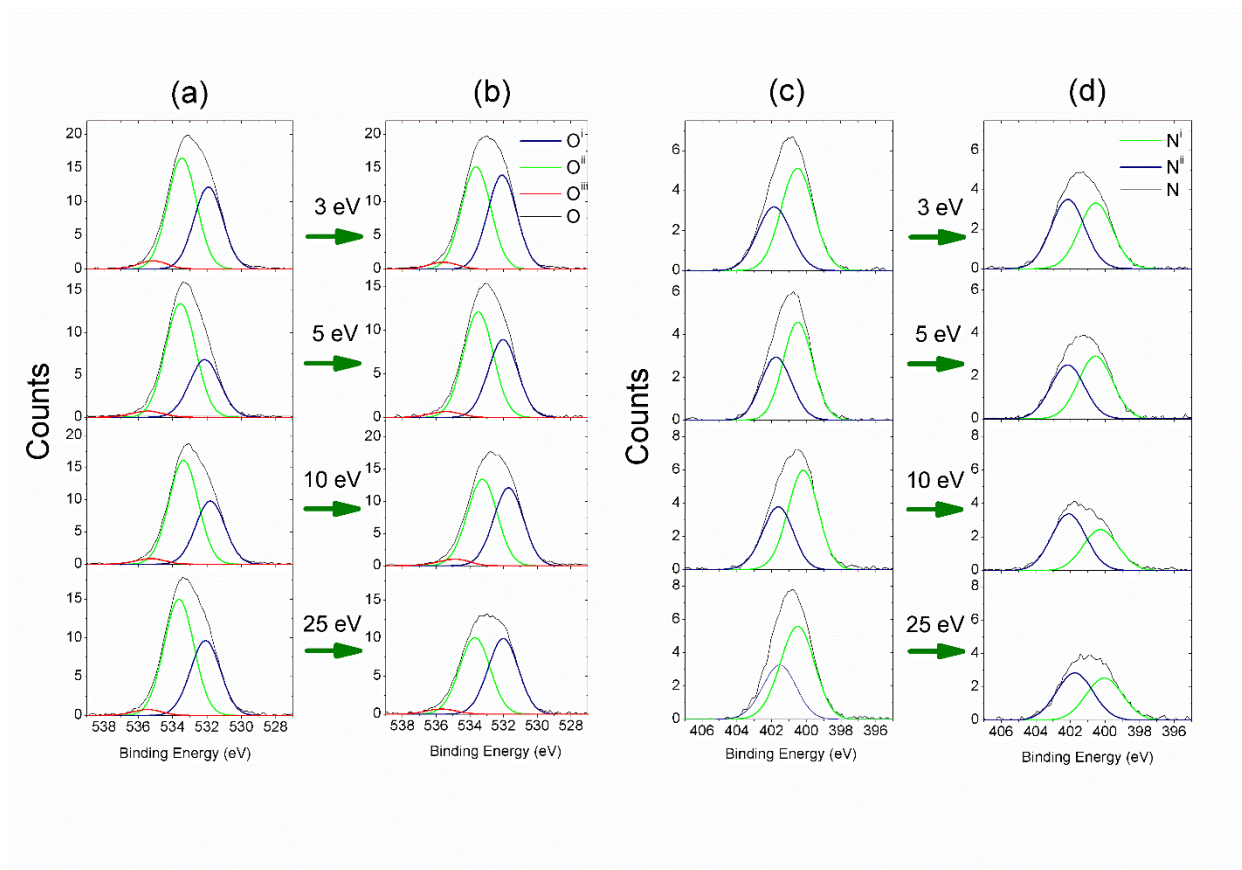


Figure S1: O-1s and N-1s photoelectron spectra before (a and c) and after (b and d) irradiation with electrons of energies (from top to bottom) 3, 5, 10 and 25 eV. Each spectrum is averaged over 3 independent measurements.

Table 1 : List of energy ranges of resonances in the constituent units of dAMP, namely, adenine, deoxyribose and phosphate analogues observed in previous experiments. Under each energy range, the observed anions or other relevant features are listed.

Molecule	Phase	0 – 2.5 eV	3 – 5 eV	4 – 7 eV	7 – 9 eV	9.5 – 11.5 eV
Adenine	Gas ^{1,2}	(A–H) [–] , (A–2H) [–] , (A–3H) [–] , (A–NH ₂) [–] , (A–NH ₃) [–]		(A–2H) [–] , (A–3H) [–] , (A–NH ₂) [–] , (A–NH ₃) [–] , C ₅ HN ₄ [–] , C ₄ H ₄ N ₄ [–] , C ₄ H ₃ N ₄ [–] , etc.		(A–2H) [–] , (A–3H) [–] , C ₅ HN ₄ [–] , C ₄ H ₃ N ₄ [–] , HC (CN) ₂ [–] , CHN ₂ [–] , C ₂ H ₃ N [–] , CN [–] , H [–]
	Condensed ³		Peak in vibrational cross-section	Electronically excited states		
	Condensed ⁴					CN [–] , H [–]
2-deoxy-D-ribose (deoxyribose)	Gas ⁵	(D–H) [–] , C ₅ H ₇ O ₃ [–] , C ₅ H ₆ O ₂ [–] , C ₅ H ₅ O ₂ [–] , C ₃ H ₅ O ₃ [–] , C ₄ H ₄ O ₂ [–]		C ₃ H ₅ O ₃ [–]		
Tetrahydrofuran (THF)	Gas ^{6,7}	(THF–2H) [–]		Peak in DEA cross-section	C ₂ HO [–]	
	Condensed ⁸				H [–]	H [–]
Dibutyl phosphate (DBP)	Gas ⁹	(DBP–H) [–] , OH [–] , H ₂ PO ₃ [–] , PO ₃ [–] , PO [–]				
Sodium dihydrogen phosphate (NaH ₂ PO ₄)	Condensed ¹⁰			O [–] , OH [–]	H [–] , O [–] , OH [–]	H [–] , O [–] , OH [–]

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