Supporting Information for

Modelling photoionisation in tautomeric DNA nucleobase derivatives 7H-adenine and 7H-guanine: ultrafast decay and photostability

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Table S1. Vertical ionisation potentials (in eV) computed with different CASPT2 zeroth-order Hamiltonians for 7H-adenine, together with their averaged estimate and standard deviation.

		$^2\pi_H^+$	$^2n_N^+$	$^2\pi_{H-1}^+$	$^2n_{N2}^+$
CASPT2	IPEA = 0.0	8.75	9.05	9.47	10.07
	IPEA = 0.25	8.93	9.25	9.64	10.29
MS-CASPT2	IPEA = 0.0	8.83	9.19	9.63	10.22
	IPEA = 0.25	9.01	9.36	9.75	10.41
XMS-CASPT2	IPEA = 0.0	9.09	9.48	9.97	10.53
	IPEA = 0.25	9.28	9.67	10.10	10.74
Average	-	**8.98**	**9.33**	**9.76**	**10.38**
Std Dev	-	0.19	0.22	0.23	0.24

Table S2. Vertical ionisation potentials (in eV) computed with different CASPT2 zeroth-order Hamiltonians for 7H-guanine, together with their averaged estimate and standard deviation.

		$^2\pi_H^+$	$^2n_O^+$	$^2\pi_{H-1}^+$	$^2n_N^+$
CASPT2	IPEA = 0.0	8.15	9.59	9.70	9.74
	IPEA = 0.25	8.32	9.82	9.90	10.01
MS-CASPT2	IPEA = 0.0	8.31	9.62	9.86	10.07
	IPEA = 0.25	8.43	9.83	10.00	10.27
XMS-CASPT2	IPEA = 0.0	8.62	9.67	10.15	10.61
	IPEA = 0.25	8.76	9.92	10.33	10.82
Average	-	**8.43**	**9.74**	**9.99**	**10.25**
Std Dev	-	0.22	0.13	0.23	0.40

Table S3. Off-diagonal elements of the effective multistate (MS) and extended multistate (XMS) CASPT2 Hamiltonian for 7H-adenine with a 18in13 full valence active space.

	MS		XMS	
	IPEA=0.0	IPEA=0.25	IPEA=0.0	IPEA=0.25
$^2\pi_H^+/^2n_N^+$	0.0028	0.0023	0.0054	0.0043
$^2\pi_H^+/^2\pi_{H-1}^+$	-0.0009	-0.0008	-0.0011	-0.0010
$^2\pi_H^+/^2n_{N2}^+$	0.0013	0.0011	0.0001	0.0001
$^2n_N^+/^2\pi_{H-1}^+$	0.0013	0.0010	0.0008	0.0007
$^2n_N^+/^2n_{N2}^+$	-0.0003	-0.0002	-0.0002	-0.0002
$^2\pi_{H-1}^+/^2n_{N2}^+$	-0.0025	-0.0021	-0.0014	-0.0014

Table S4. Off-diagonal elements of the effective extended multistate (MS) and extended multistate (XMS) CASPT2 Hamiltonian for 7H-adenine with a reduced 16in9 active space.

	XMS
	IPEA=0.0
$^2\pi_H{}^+/^2n_N{}^+$	-0.0008
$^2\pi_H{}^+/^2\pi_{H-1}{}^+$	-0.0008
$^2\pi_H{}^+/^2n_{N2}{}^+$	0.0024
$^2n_N{}^+/^2\pi_{H-1}{}^+$	0.0015
$^2n_N{}^+/^2n_{N2}{}^+$	-0.0180
$^2\pi_{H-1}{}^+/^2n_{N2}{}^+$	-0.0012

Table S5. Contributions (weights, in %) of the different configuration state functions (CSFs), represented by the orbital where the unpaired electron sits, towards describing the perturbed modified multistate (MS) and extended multistate (XMS) wave functions of the cationic states in 7H-adenine.

		MS		XMS	
	CSF	IPEA=0.0	IPEA=0.25	IPEA=0.0	IPEA=0.25
$^2\pi_H{}^+$	π_H	0.62	0.64	0.59	0.62
	π_{H-1}	0.11	0.10	0.15	0.13
$^2n_N{}^+$	n_N	0.67	0.67	0.66	0.66
	n_{N2}	0.10	0.11	0.12	0.12
$^2\pi_{H-1}{}^+$	π_H	0.12	0.11	0.17	0.14
	π_{H-1}	0.68	0.69	0.63	0.65
$^2n_{N2}{}^+$	n_N	0.11	0.11	0.12	0.12
	n_{N2}	0.66	0.65	0.63	0.63

Table S6. Off-diagonal elements of the effective multistate (MS) and extended multistate (XMS) CASPT2 Hamiltonian for 7H-guanine with a 20in14 full valence active space.

	MS		XMS	
	IPEA=0.0	IPEA=0.25	IPEA=0.0	IPEA=0.25
$^2\pi_H{}^+/^2n_O{}^+$	-0.0042	-0.0036	-0.0040	-0.0032
$^2\pi_H{}^+/^2\pi_{H-1}{}^+$	0.0005	0.0003	-0.0010	-0.0010
$^2\pi_H{}^+/^2n_N{}^+$	-0.0010	-0.0010	0.0000	0.0000
$^2n_O{}^+/^2\pi_{H-1}{}^+$	-0.0006	0.0004	-0.0004	-0.0001
$^2n_O{}^+/^2n_N{}^+$	-0.0027	-0.0030	-0.0005	-0.0004
$^2\pi_{H-1}{}^+/^2n_N{}^+$	-0.0073	-0.0068	-0.0065	-0.0057

Table S7. Off-diagonal elements of the effective extended multistate (MS) and extended multistate (XMS) CASPT2 Hamiltonian for 7H-guanine with a reduced 16in9 active space.

	XMS
	IPEA=0.0
$^2\pi_H{}^+/^2n_O{}^+$	-0.0053
$^2\pi_H{}^+/^2\pi_{H-1}{}^+$	0.0001
$^2\pi_H{}^+/^2n_N{}^+$	0.0044
$^2n_O{}^+/^2\pi_{H-1}{}^+$	-0.0006
$^2n_O{}^+/^2n_N{}^+$	0.0052
$^2\pi_{H-1}{}^+/^2n_N{}^+$	-0.0003

Table S8. Contributions (weights, in %) of the different configuration state functions (CSFs), represented by the orbital where the unpaired electron sits, towards describing the perturbed modified multistate (MS) and extended multistate (XMS) wave functions of the cationic states in 7H-guanine.

		MS		XMS	
	CSF	IPEA=0.0	IPEA=0.25	IPEA=0.0	IPEA=0.25
$^2\pi_H{}^+$	π_H	0.77	0.78	0.77	0.78
$^2n_O{}^+$	n_O	0.54	0.57	0.70	0.70
	n_N	0.23	0.20	0.02	0.02
$^2\pi_{H-1}{}^+$	π_{H-1}	0.71	0.71	0.69	0.70
$^2n_N{}^+$	n_O	0.21	0.18	0.01	0.01
	n_N	0.51	0.53	0.73	0.73