Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Ultrafast Structural Dynamics of Photoexcited Adenine

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Figures

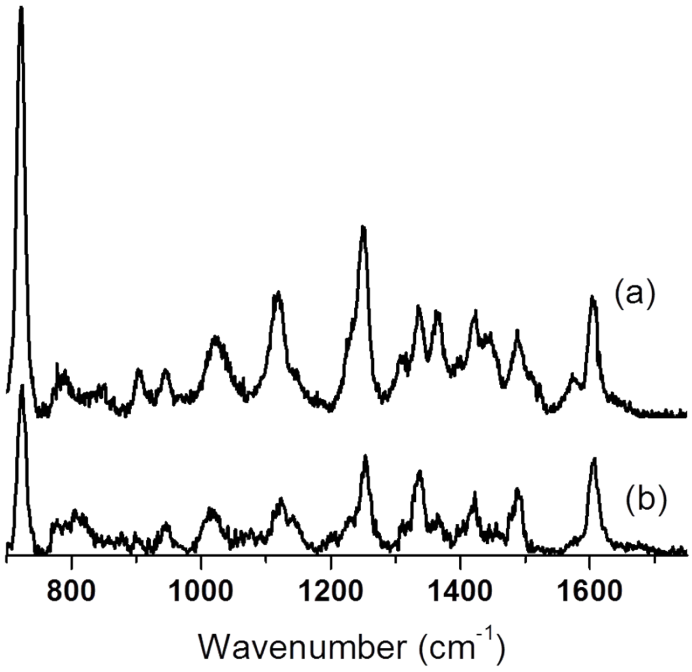

Figure S1. (a) Parallel polarized and (b) depolarized RR spectra of aqueous adenine with 215 nm laser excitation. Incident laser power on sample was was 0.6 mw and sample concentration was 2 mM in miliQ water.

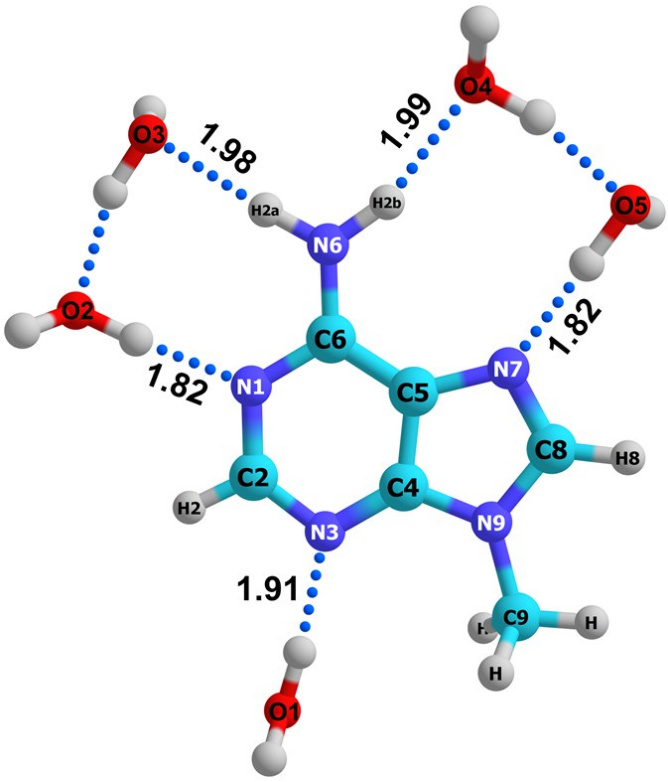

Figure S2. Optimized structure of neutral 9-meA in solution as 9-meA•5H_2O complex at B3LYP/6-311+G(2d,p)//PCM level of theory used for computation of excited states. All H bond distances (in Å) between water molecules and base along with conventional numbering of ring atoms are mentioned.

Tables

Table S1. XYZ Coordinates (Å) of energy optimized ground state structure of Ade•6H_2O complex[a].

	X	Y	Z
N	-0.639046000	-1.670515000	-0.028895000
C	0.643912000	-2.044287000	-0.038467000
N	1.720960000	-1.267509000	-0.027117000
C	1.404043000	0.039761000	-0.006069000
C	0.115325000	0.569346000	0.001485000
C	-0.960949000	-0.350377000	-0.008857000
N	2.252202000	1.112815000	0.008926000
C	1.467365000	2.225899000	0.023605000
N	0.180502000	1.953702000	0.019247000
H	1.888174000	3.219130000	0.036620000
H	3.283446000	1.075320000	0.012256000
O	-4.487561000	-1.998646000	0.011294000
H	-5.017496000	-2.047503000	-0.792780000
H	-3.892883000	-2.781623000	-0.011981000
O	4.433529000	-1.994984000	-0.106901000
H	3.455115000	-1.846561000	-0.049710000
H	4.664097000	-2.544370000	0.651641000
O	-1.516480000	4.184113000	-0.011133000
H	-0.909061000	3.401079000	-0.030373000
H	-1.360799000	4.660795000	-0.835009000
O	5.052399000	0.678353000	-0.041101000
H	5.561808000	0.941270000	0.734648000
H	4.996826000	-0.305518000	-0.009236000
N	-2.248265000	0.000281000	-0.000447000
H	-2.977289000	-0.711913000	-0.018078000
H	-2.553445000	0.970446000	0.029622000
H	0.822323000	-3.114267000	-0.057106000
O	-2.440652000	-3.824415000	-0.014541000
H	-2.303579000	-4.331115000	0.794588000
H	-1.778292000	-3.085129000	0.009512000
O	-3.728827000	2.577174000	0.039222000
H	-4.226702000	2.709583000	0.854177000
H	-3.034166000	3.274145000	0.034310000

[a]computed at B3LYP/6-311+G(2d,p)//PCM level

Table S2. Experimental and computed vibrational wavenumbers, PED, normal mode description, dimensionless displacements and internal reorganization energies for all RR modes of adenine.

Exp. wavenum. (cm^{-1})	Comp[a] wavenum. (cm^{-1})	PED[b] (%)	Mode description	$\|\Delta\|$[c]	λ_{int}[d] (cm^{-1})
1602	1624	str N3C4 (12) - be C5N7C8 (11) - H9N9C8 (14) - C4N9C8 (13)	Pyr str	0.32	81.3
1486	1527	- str N7C8 (14) + N6C6 (24) + be C8H (13)	Pyr breath + Imid str	0.221	36.4
1440	1499	- str N7C8 (17) - N3C2 (10) + N1C6 (11) - be C2H (10) - C4N9C8 (10)	In-plane purine def	0.220	34.8
1420	1438	- str N6C6 (11) - N9C4 (26) + be C5N7C8 (22)	In-plane purine def	0.31	68.1
1402	1381	be C2H (20)	Pyr breath	0.11	8.8
1364	1485	- str N9C8 (12) + be H9N9C8 (39) + C2H (21)	CH and NH be	0.27	49.1
1333	1358	str N1C2 (39) + N7C5 (11)	Pyr def	0.30	60.9
1309	1337	str N3C2 (37) + N7C5 (13) - be N1C2N3 (15)	Pyr def	0.20	25.6
1251	1284	str N7C8 (27) + N1C2 (10) + be C8H (29)	Imid def	0.37	83.7
1231	1243	str N7C5 (32) - be N6C6C5 (10) + C6N6H6a (12)	Rock NH_2	0.19	21.3
1142	1143	str N9C8 (13) + be C5N7C8 (21) - C8H (24)	Pyr breath	0.17	16.5
1120	1176	str N9C8 (39) - be N7C8N9 (11)	Imid def	0.51	145.9
1021	1029	str N1C6 (32) + rock NH_2 (16)	Rock NH_2	0.39	76.2
904	923	- be C6N1C2 (10) + N1C2N3 (20) + C4N9C8 (13)	In-plane pyr def	0.31	42.5
725	742	- str N3C4 (12)	In-phase pyr + imid breath	0.80	230.0
				Total	981

[a] without scaling and computed at B3LYP/6-311+G(2d,p) level on N9H-Ade•$6H_2O$ complex with PCM solvation; [b]Potential energy distributions (PEDs) of each normal mode computed using VEDA 4.0 program, sign indicates relative phase of movement of internal coordinates; [c]best-fitted dimensionless Δ's for all RR active modes of adenine with parameters described in Table 2; [d]mode specific internal reorganization energies calculated using the relation, $\lambda_k=(\Delta_k^2\omega_k)/2$; Abbreviations, str, bond stretching; be, angle bending; out, out of plane motion; tors, torsional vibration and rock, rocking motion of exocyclic amino group; def, in-plane ring deformation; breath, ring breathing; rock, rocking motion; Pyr, pyrimidine ring; Imid, imidazole ring.

Table S3. Depolarization ratios for Raman bands of adenine obtained at excitation wavelength of 215 nm.

RR Band (cm^{-1})	Depolarization ratio (ρ)
725	0.33
1021	0.34
1120	0.28
1142	0.38
1231	0.33
1251	0.37
1309	0.31
1333	0.49
1364	0.18
1402	0.33
1420	0.31
1486	0.60
1602	0.51

Table S4. XYZ Coordinates (Å) of energy optimized ground state structure of 9-meA•5H_2O complex[a].

	X	Y	Z
N	-0.297237000	-1.678546000	-0.028057000
C	1.017778000	-1.916379000	-0.033895000
N	2.010277000	-1.032835000	-0.019907000
C	1.557242000	0.231460000	-0.001269000
C	0.221103000	0.626280000	0.003181000
C	-0.754734000	-0.399443000	-0.007994000
N	2.295054000	1.387902000	0.014014000
C	1.391994000	2.412204000	0.025601000
N	0.141651000	2.008117000	0.019105000
H	1.710470000	3.443287000	0.037533000
O	-4.086714000	-2.405311000	0.012249000
H	-4.615343000	-2.502440000	-0.788278000
H	-3.414365000	-3.122320000	-0.022060000
O	4.634442000	-2.219435000	-0.090229000
H	3.762502000	-1.769361000	-0.038669000
H	4.909785000	-2.339418000	0.825531000
O	-1.778346000	4.057646000	-0.034344000
H	-1.094161000	3.341764000	-0.046860000
H	-1.680875000	4.532127000	-0.868388000
N	-2.071295000	-0.183694000	-0.000767000
H	-2.722508000	-0.967880000	-0.015980000
H	-2.475492000	0.749395000	0.036502000
H	1.305373000	-2.962441000	-0.051330000
O	-1.863913000	-4.009425000	-0.044403000
H	-1.671030000	-4.512285000	0.755704000
H	-1.282154000	-3.205633000	-0.009704000
O	-3.807268000	2.225476000	0.065999000
H	-4.301717000	2.310282000	0.889373000
H	-3.191787000	2.992780000	0.043861000
C	3.748583000	1.498618000	0.018956000
H	4.156946000	1.024316000	0.910247000
H	4.162392000	1.020695000	-0.867659000
H	4.015414000	2.552482000	0.017802000

[a]computed at B3LYP/6-311+G(2d,p)//PCM level.

Table S5. Experimental and computed wavenumbers and PEDs of vibrational modes of 9-meA.

RR, Solution, 257 nm [1]	Raman, Solid, 514.5 nm [2]	IR, in Ar matrix [3]	SERS [4]	Comp. Freq [5]	IR-UV ion-dip, Freq [6]	Comp. Freq, (Scaled by 0.983) [6]	Comp. Freq, 9-meA [a]	Comp. Freq, 9-meA + $5H_2O$ [b]	PED (%) [c]	Assignment
cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}		
1680	1680	1632		1630	1632	1627	1636	1694	be $H_{6b}N_6H_{6a}$ (80)	δ_{Sciss} NH_2
1603	1573	1596	1597	1592	1599	1593	1596	1595	str N_3C_4 (24) - N_9C_4 (10)	ν (N_3-C_4) + ν (N_7-C_8) + δ_{Rock} NH_2
1537	1526		1568	1575		1579	1610	1622	- str N_3C_2 (17) - be $C_6N_1C_2$ (15) + $C_4N_9C_8$ (11) - $N_3C_4C_5$ (10) + $C_5N_7C_8$ (10)	
		1511	1524	1513	1515	1507	1533	1547	str N_7C_8 (10) - N_6C_6 (13) + be $C_4N_9C_8$ (13) - $H_8C_8N_7$ (13)	ν (N_7-C_8) + ν (N_9-C_9)
1498	1517	1483		1494		1489	1506	1506	be $HC_{me}H$ (23)	δ C_2H + CH_3 def + Pyr def
		1449		1486	1450	1456	1475	1478	- be $HC_{me}H$ (38) + $HC_{me}H$ (39) + tor $HC_{me}N_9C_8$ (15)	CH_3 def
		1476	1460		1470	1473	1492	1505	be $H_2C_2N_1$ (18) + $HC_{me}H$ (34)	δ C_2H + CH_3 def + ν (C_6-N_1) + ν (C_2-N_3)
1437		1435		1437	1429	1439	1458	1460	- be $HC_{me}H$ (38) + $HC_{me}H$ (39) + tor $HC_{me}N_9C_8$ (15)	CH_3 def + ν (N_7-C_8)
		1411	1406		1414	1415	1429	1441	str N_6C_6 (10) - N_9C_4 (18) - be C_2H_2 (12) + $C_5N_7C_8$ (16)	
		1370			1369	1369	1390	1398	- str N_9C_4 (11) + be C_2H_2 (28)	
1343		1328	1329	1338	1327	1336	1351	1360	str N_1C_2 (30) + N_7C_5 (11) - be $C_5N_7C_8$ (11)	
		1344			1345	1341	1361	1377	str N_9C_8 (28)	Ring Def + ν (C_8-N_9)
		1295			1292	1307	1323	1335	str N_3C_2 (31) - N_3C_4 (10) + N_7C_5 (13)	
1254	1256	1254	1242	1257	1256	1254	1274	1280	str N_1C_2 (10) - N_7C_5 (11) + be $H_8C_8N_7$ (31)	
1208	1230	1234		1230	1232	1241	1262	1264	str N_7C_8 (12)	
					1199	1199	1216	1218	str N_7C_5 (22) + be $H_8C_8N_7$ (14)	
			1113		1136	1131	1151	1153	be $HC_{me}H$ (17) - $HC_{me}H$ (17) - tor	CH_3 def

									$HC_{me}N_9C_8$ (54)	
					1067	1055	1077	1092	str N_9C_8 (12) + be $C_2N_3C_4$ (12)	δ_{rock} NH_2 + CH_3 def
1010	1047	1044		1043	1036	1041	1061	1073	be $N_9C_8N_7$ (23) + tor $HC_{me}N_9C_8$ (13) - $HC_{me}N_9C_8$ (13)	δ_{rock} NH_2 + Imd def + CH_3 def + ν (C_8-N_9)
			1015		1000	984	1004	1017	str N_1C_6 (32) + be $H_{2b}N_2O_3$ (11)	
		944	958		958	961	975	980	tor $H_2C_2HN_3$ (77) - $N_1C_2N_3C_4$ (10)	γ C_2H
		894			895	892	908	935	be $N_1C_2N_3$ (22)	Ring def
		843			841	838	873	877	- tor $H_8C_8HO_5$ (71) - $C_4N_9C_8N_7$ (13)	γ C_8H
		800			800	796	820	824	tor $N_1C_2N_3C_4$ (17) - $C_6N_1C_2N_3$ (15) - $C_5N_7C_8N_9$ (18) - out $N_3N_9C_5C_4$ (23)	τ_{def} (Pyr + Imd)
728			735	731	730	734	745	758	str N_9C_8 (13) + N_9C_{me} (19) + be $N_9C_8N_7$ (11)	τ_{def} (Pyr + Imd) + ν (N_9-C_9)
				714	715	718	726	723	be O1HN3 (12)	
		681			673	679	691	700	- tor $H_{6a}N_6C_6C_5$ (12) - $H_{6b}N_6H_{6a}O_3$ (11) - $C_2N_3C_4N_9$ (10) - $N_1C_2N_3C_4$ (13) - $C_6N_1C_2N_3$ (11) + out $N_3N_9C_5C_4$ (17)	τ Ring
601		645	620	645	640	650	658	655	tor $C_5N_7C_8N_9$ (46)	τ Ring
		581		588	577	578	590	606	be $N_6C_6C_5$ (13) + $H_{2b}N_2O_3$ (13)	τ NH_2
		575		563	553	558	570	569	- tor $N_1C_2N_3C_4$ (16) + $C_6N_1C_2N_3$ (19) - $C_4N_9C_8N_7$ (19) - out $N_6N_1C_5C_6$ (14)	
535	542		536	552		532	544	552	str N_9C_4 (11) + N_9C_{me} (14) - be $C_4N_9C_8$ (11) + $C_2N_3C_4$ (21) - $C_{me}N_9C_4$ (13)	Ring def
				529		523	531	542	be $C_6N_1C_2$ (16) - $C_2N_3C_4$ (12) + $N_1C_2N_3$ (10)	

[1] Ref 1, RR with 257 nm excitation of aqueous solution at pH 7; [2] Ref 2, FT-IR, and Raman with 514.5 nm laser on polycrystalline state of 9-meA; [3] Ref 3, FT-IR spectra of 9-meA in Ar gas matrix; [4] Ref 4, Surface enhanced Raman scattering (SERS) of adsorbed 9-meA on Ag electrode with 514.5 nm excitation; [5] Ref 5, computed at B3LY/6-31G(d)//gas level of theory, and using scaled quantum mechanical (SQM) method described there in; [6] Ref 6, computed at B3LY/6-311++G(df, pd)//gas level and scaled by 0.983; [a, b] this work, computed on isolated 9-meA [a], and 9-meA + 5 H_2O complex [b] at B3LYP/6-311+G(2d,p)//PCM level and are not scaled; [c] this work, PEDs are computed on energy optimized 9-meA + 5 H_2O complex using VEDA 4.0 program (Ref 7). Abreviations: PED =

Potential Energy Distribution; ν = bond stretching; δ, be = in-plane bending, γ, out = out of plane bending; τ, tors = out of plane torsion; sciss = scissoring; rock = rocking motion; Pyr = pyrrole ring; Imd = imidazole ring; def = ring deformation; twist = twisting motion. Negative sign in front of a contribution in PED indicate out of phase vibration with respect to that with positive sign.

Table S6. Computed sign of deltas for intense RR bands of Ade with B3LYP and CAM-B3LYP functional on B_b state.

Vibrational Frequencies (cm^{-1})		Sign of Δs	
Experimental	Computed[a]	B3LYP[b]	CAM-B3LYP[c]
725	742	1	1
1021	1029	-1	-1
1120	1176	-1	-1
1251	1284	1	1
1333	1358	-1	-1
1420	1438	1	1
1364	1485	1	1
1486	1527	1	1
1602	1624	1	1

[a]computed at B3LYP/6-311+G(2d,p)//PCM level and are not scaled; Sign of gradients are obtained with computed cartesian gradients on B_b electronic state with [b]TD-B3LYP and with [c]TD-CAM-B3LYP method. Gradients with both the methods are calculated on optimized ground state geometry and normal modes of Ade•$6H_2O$ complex with at B3LYP/6-311+G(2d,p)//PCM method.

Details of computational methods

Explicit water molecules are included to account for non-covalent interactions that seem important in several studies; decay of photoexcited Ade,[8,9] computation of pKa values,[10] and prediction of vibrational frequencies.[11] Use of such treatment along with continuum type bulk solvation (PCM) is known as cluster-continuum model.[12] B3LYP functional has been extensively used for computation of vibrational frequencies of nucleobase systems.[11,13–17] We obtained good agreement between computed and experimental wavenumbers, and the predicted normal modes are in agreement with the comprehensive vibrational assignment of Ade performed by McNaughton and coworkers.[18] Though the normal modes computed on Ade•$6H_2O$ complex are similar to those calculated on isolated N_9H-Ade,[18] subtle differences in the composition of the potential energy distributions (PED) are expected. These differences arise from the directional H-bonding interactions at N1, N3, N7, N9-H sites, and with the -NH_2 moiety with explicit water molecules. Though, these interactions do not drastically change the composition of PEDs, but alters relative contribution from individual internal coordinates.

9-meA is a model of N_9H-Ade

Both, Ade and 9-meA have the same UV absorbing chromophore, differing with respect to the N9 substituent which is a methyl moiety in the latter case in place of a hydrogen atom in the former. Following the 267 nm excitation, non-radiative relaxation of 9-meA and Ade are found to be very similar with sub-ps decay constants[8,19] Due to change in substitution at the N9 site, the positions of fundamental vibrations of Ade differ minutely from those of 9-meA.[1,3,4,20] Methyl group which is heavier than hydrogen atom alters PEDs of normal modes that are primarily localized on the imidazole ring of Ade.

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