Supplementary Information

Unveiling the complex vibronic structure of canonical adenine cation

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Table S1: Total energies (in Hartrees) and ionization energies (IE in eV) at the (R)CCSD(T)-F12(b)/cc-pVTZ-F12 (+CV+SR+ZPVE) level. ZPVE corresponds to the zero point vibrational energy (in cm^{-1}).

Species	9H-adenine	9H-adenine$^+$	3H-adenine	3H-adenine$^+$	7H-adenine	7H-adenine$^+$
Total energies						
PBE0/aug-cc-pVDZ	-466.87444	-466.57908	-466.86206	-466.56945	-466.86187	-466.55799
ZPVE [a]	24738	24828	24865	24768	24771	24650
CCSD(T)-F12b/cc-pVTZ-F12	-466.73389	-466.43108	-466.72056	-466.42223	-466.72200	-466.41086
CCSD(T,fc)/cc-pwCVTZ	-466.57363	-466.27777	-466.55994	-466.26894	-466.56182	-466.25734
CCSD(T,full)/cc-pwCVTZ	-467.07047	-466.77404	-467.05671	-466.76506	-467.05849	-466.75351
CCSD(T)/cc-pVTZ	-466.54498	-466.24939	-466.53130	-466.24060	-466.53316	-466.22896
CCSD(T)/cc-pVTZ-DK	-466.76288	-466.46745	-466.74922	-466.45867	-466.75111	-466.44704
Ionization energies(in eV)						
CCSD(T)-F12b	8.240		8.118		8.467	
CV	0.016		0.018		0.014	
SR	-0.004		-0.004		-0.004	
ZPVE	0.011		-0.012		-0.015	
IE(F12b+CV+SR+ZPVE)	8.262		8.120		8.462	

[a] Based on harmonic vibrational frequencies at PBE/aug-cc-pVDZ level.

Table S2(a): B3LYP/aug-cc-pVDZ harmonic frequencies (in cm^{-1}) of ground state ($\widetilde{X}^2A''$) of 9-adenine$^+$. (In plane vibration: ν stretching, β bending, δ deformation. Out of plane vibration: γ wagging, η twisting, τ torsion.).

No.	Symm.	Harm.	Assignment	No.	Symm.	Harm.	Assignment
1	a'	**3668**	ν NH	21	a'	**917**	δ (N_7 C_8N_9)
2	a'	**3562**	ν NH	22	a'	**879**	δ (N_1 C_2N_3), δ ring
3	a'	**3530**	ν NH	23	a'	**727**	δ ring
4	a'	**3246**	ν CH	24	a'	**598**	δ ring
5	a'	**3186**	ν CH	25	a'	**512**	δ ring
6	a'	**1669**	β NH, $\nu(C_6N_{10})$	26	a'	**506**	δ (C_5 C_6N_1), δ ring
7	a'	**1637**	$\nu(N_3C_4)$, $\nu(C_6N_{10})$	27	a'	**280**	$\delta(C_5C_6N_{10})$
8	a'	**1567**	β NH, δ ring	28	a''	**988**	β NH_2
9	a'	**1502**	β NH, $\nu(C_6N_{10})$	29	a''	**935**	γ C_8H_{15}
10	a'	**1451**	β CH, $\nu(C_4C_5)$	30	a''	**827**	τ ring
11	a'	**1435**	β N_9H_{14}, β C_2H_{13} , $\nu(C_8N_9)$, $\nu(N_7C_8)$	31	a''	**718**	γ NH
12	a'	**1416**	β $C_2H_{13,}$ $\nu(C_2N_3)$, $\nu(N_7C_5)$, β NH	32	a''	**669**	γ NH
13	a'	**1413**	$\nu(C_6N_1)$, $\nu(N_1C_2)$, $\nu(N_3C_4)$	33	a''	**660**	γ NH
14	a'	**1383**	β CH, $\nu(C_4C_5)$, δ ring	34	a''	**613**	η NH
15	a'	**1313**	β CH, β NH_2, $\nu(N_7C_8)$, δ ring	35	a''	**565**	γ CH, τ ring
16	a'	**1207**	β CH, $\nu(N_7C_8)$, δ ring	36	a''	**448**	γ CH, τ ring
17	a'	**1187**	δ ring, $\nu(N_3C_2)$, β NH_2	37	a''	**276**	τ ring, γ NH,,γ CH
18	a'	**1115**	β NH, β CH, $\nu(N_9C_8)$,	38	a''	**222**	τ ring, γ NH,γ CH
19	a'	**1096**	β NH, δ ring, $\nu(N_3C_2)$, $\nu(N_9C_4)$	39	a''	**143**	τ ring, γ NH
20	a'	**997**	γ C_2H_{10}				

Table S2(b): Relative intensities with respect the calculated 0_0^0 transition intensity and energy position of the bands for the 9A($\tilde{X}^1A'$) → 9A$^+$($\tilde{X}^2A''$) simulated transitions. The 0_0^0 transition energy is set to the adiabatic ionization energy of 9A (= 8. 262 eV). I(0_0^0) is set equal to 1.

Transition	Assignment	v	Energy (eV)	Rel.I
39_0^2	τ ring, γ NH	2	8.298	0.078
24_0^1	δ ring	1	8.337	0.184
23_0^1	δ ring	1	8.353	0.071
36_0^2	γ CH, τ ring	2	8.374	0.112
19_0^1	β NH, δ ring, $\nu(N_3C_2)$, $\nu(N_9C_4)$	1	8.400	0.088
34_0^2	η NH	2	8.415	0.540
33_0^2	γ NH	2	8.427	0.455
14_0^1	β CH, $\nu(C_4C_5)$, δ ring	1	8.435	0.078
13_0^1	$\nu(C_6N_1)$, $\nu(N_1C_2)$, $\nu(N_3C_4)$	1	8.439	0.097
9_0^1	β NH, $\nu(C_6N_{10})$	1	8.450	0.344
7_0^1	$\nu(N_3C_4)$, $\nu(C_6N_{10})$	1	8.466	0.080
6_0^1	β NH, $\nu(C_6N_{10})$	1	8.471	0.118
$33_0^2 38_0^2$	τ ring, γ NH,γ CH / γ NH	2/2	8.483	0.076
$24_0^1 34_0^2$	δ ring/ η NH	2/1	8.491	0.061
$24_0^1 33_0^2$	δ ring,/ γ NH	1/2	8.502	0.052
$34_0^2 36_0^2$	γ CH, τ ring/ η NH	2/2	8.529	0.067
$33_0^2 36_0^2$	γ CH, τ ring/ γ NH	2/2	8.539	0.065
34_0^4	η NH	4	8.569	0.148
33_0^4	γ NH	4	8.592	0.180
$9_0^1 34_0^2$	η NH/ β NH, $\nu(C_6N_{10})$	2/1	8.791	0.184
$9_0^1 33_0^2$	γ NH/ β NH, $\nu(C_6N_{10})$	2/1	8.803	0.155

Figure S1: Optimized structure of singlet 9H-adenine (X^1A') obtained at PBE0/aug-cc-pVDZ level. The numbering of the atoms used in the tables is also given.

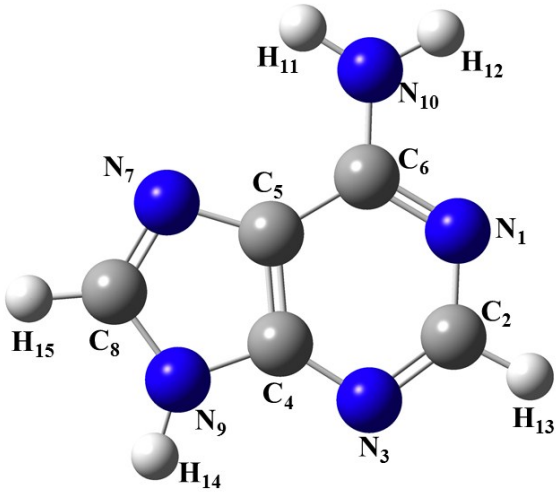

Table S3: Main geometrical parameters (Å and degrees) of the neutral and cation of 9H-adenine and 9H-adenine$^+$, obtained at PBE0/aug-cc-pVDZ level of theory. The main geometrical changes between neutral and ionic 9H-adenine are in bold.

Bonds and Angles	9-adenine (X^1A')	9-adenine$^+$ (X^2A'')
N_1-C_2	**1.340**	**1.314**
C_2-N_3	**1.332**	**1.377**
N_3-C_4	**1.336**	**1.301**
C_4-C_5	**1.396**	**1.429**
C_5-C_6	**1.409**	**1.434**
C_6-N_1	1.340	1.353
C_6-N_{10}	**1.349**	**1.320**
C_5-N_7	**1.380**	**1.336**
N_7-C_8	**1.309**	**1.344**
C_8-N_9	1.374	1.350
N_9-C_4	1.372	1.381
N_{10}-H_{11}	1.006	1.014
N_{10}-H_{12}	1.007	1.015
C_2-H_{13}	1.092	1.091
C_8-H_{15}	1.086	1.087
N_9-H_{14}	1.009	1.014
N_1-C_2-N_3	128.9	128.5
C_2-N_3-C_4	111.1	112.4
N_3-C_4-C_5	127.0	126.5
C_4-C_5-C_6	115.8	115.0
C_5-C_6-N_1	118.7	118.9
C_5-C_6-N_{10}	122.3	122.2
C_4-C_5-N_7	111.4	111.9
C_5-N_7-C_8	103.9	103.9
N_7-C_8-N_9	113.4	113.7
C_8-N_9-C_4	106.8	106.8

Table S4: Main geometrical parameters (Å and degrees) of the ground state ($\tilde{X}^2A''$) and first two excited states ($1^2A'$, $2^2A''$) of 9-adenine$^+$ and 9-adenine, obtained at SA-CASSCF/aug-cc-pVDZ level of theory using C_1 symmetry.

Bonds and Angles	9H-adenine$^+$ (X^2A'')	9H-adenine$^+$ ($1^2A'$)		9H-adenine$^+$ ($2^2A''$)
		C_s	C_1	
N_1-C_2	1.322	1.352	1.370	1.418
C_2-N_3	1.362	1.292	1.284	1.264
N_3-C_4	1.278	1.334	1.345	1.371
C_4-C_5	1.444	1.400	1.391	1.384
C_5-C_6	1.449	1.402	1.405	1.391
C_6-N_1	1.339	1.346	1.365	1.409
C_6-N_{10}	1.305	1.323	1.312	1.302
C_5-N_7	1.339	1.381	1.379	1.386
N_7-C_8	1.345	1.316	1.318	1.313
C_8-N_9	1.367	1.385	1.384	1.394
N_9-C_4	1.359	1.344	1.343	1.330
N_{10}-H_{11}	0.999	0.997	0.998	1.000
N_{10}-H_{12}	1.000	0.995	0.997	0.999
C_2-H_{13}	1.077	1.075	1.075	1.076
C_8-H_{15}	1.073	1.073	1.072	1.072
N_9-H_{14}	0.998	0.997	0.998	0.991
N_1-C_2-N_3	129.1	119.4	121.1	126.0
C_2-N_3-C_4	113.4	114.7	114.9	114.5
N_3-C_4-C_5	125.0	126.9	126.8	126.8
C_4-C_5-C_6	116.2	118.5	117.1	116.9
C_5-C_6-N_1	117.5	109.2	111.9	117.5
C_5-C_6-N_{10}	121.6	127.9	127.2	127.3
C_4-C_5-N_7	111.9	111.3	111.3	110.9
C_5-N_7-C_8	103.5	103.4	103.4	103.6
N_7-C_8-N_9	113.6	113.0	112.8	112.4
C_8-N_9-C_4	107.1	107.1	107.0	106.9

Table S5: Harmonic and anharmonic frequencies (in cm^{-1}) of 9-adenine electronic ground state obtained at PBE0/aug-cc-pVDZ level of theory. Anharmonic frequencies are arranged according to the harmonic frequencies. (In plane vibration: ν stretching, β bending, δ deformation. Out of plane vibration: γ wagging, η twisting, τ torsion.)

		9-adenine (X^1A')					**9-adenine (X^1A')**		
No.	Symm.	Harm.	Anharm.	Assignment	No.	Symm.	Harm.	Anharm.	Assignment
1	a'	3782	3485	ν NH	21	a"	987	955	γ CH
2	a'	3684	3518	ν NH	22	a'	947	932	δ ring
3	a'	3638	3390	ν NH	23	a'	903	891	δ ring
4	a'	3271	3143	ν CH	24	a"	866	846	γ CH
5	a'	3196	3069	ν CH	25	a"	823	802	τ ring, γ CH
6	a'	1693	1647	β NH, ν (C_5C_6)	26	a'	735	727	δ ring
7	a'	1674	1645	β NH, ν (C_4N_3)	27	a"	695	673	τ ring
8	a'	1620	1573	β NH, δ ring	28	a"	675	657	γ CH, γ NH
9	a'	1546	1516	β CH, ν (N_7C_8)	29	a'	619	617	δ ring, β NH
10	a'	1524	1489	β NH, β CH	30	a"	587	564	γ NH, γ CH
11	a'	1466	1429	N (N_9C_4), β NH	31	a"	552	405	γ NH
12	a'	1438	1398	β NH, β CH	32	a"	543	494	γ NH, γ CH
13	a'	1400	1363	β NH, β CH	33	a'	530	531	δ ring
14	a'	1384	1353	β CH, β NH	34	a'	519	514	β NH, β CH
15	a'	1361	1326	β CH, δ ring	35	a"	302	296	γ CH, τ ring
16	a'	1278	1256	β CH, β NH	36	a'	273	277	β NH, δ ring
17	a'	1256	1259	β CH, β NH	37	a"	222	245	τ ring, γ NH
18	a'	1159	1140	β NH, β CH	38	a"	169	201	γ NH, τ ring
19	a'	1096	1074	β NH, β CH	39	a"	49	-*	γ NH
20	a'	1015	1089	β NH, δ ring					

*Strongly anharmonic. VPT2 is not applicable.

Table S6: PBE0/aug-cc-pVDZ harmonic and anharmonic frequencies (in cm^{-1}) of ground state (X^2A'') of 9-adenine$^+$. Anharmonic frequencies are arranged according to the harmonic frequencies. Anharmonic frequencies obtained at SA-CASSCF/aug-cc-pVDZ level (closed 30, occ 40) are also listed. (In plane vibration: ν stretching, β bending, δ deformation. Out of plane vibration: γ wagging, η twisting, τ torsion.).

		9H-adenine$^+$ (X^2A'')						**9H-adenine$^+$ (X^2A'')**			
		PBE0		SA-CASSCF				PBE0		SA-CASSCF	
No.	Symm.	Harm.	Anharm.	Anharm.[a]	Assignment	No.	Symm.	Harm.	Anharm.	Anharm.[a]	Assignment
1	a'	3683	3503	3535	ν NH	21	a'	923	911	884	δ ring, β CH
2	a'	3629	3465	3492	ν NH	22	a'	885	870	843	δ ring, β CH
3	a'	3545	3386	3412	ν NH	23	a'	739	729	695	δ ring, β CH
4	a'	3277	3151	3107	ν CH	24	a'	607	600	563	δ ring, β CH
5	a'	3231	3106	3073	ν CH	25	a'	520	515	509	δ ring, β CH
6	a'	1681	1640	1685	$\nu(N_3C_4)$, $\nu(C_6N_{10})$	26	a'	504	498	477	δ ring
7	a'	1673	1633	1653	β NH, $\nu(C_6N_{10})$	27	a'	274	273	275	$\delta(C_5C_6N_{10})$
8	a'	1604	1567	1546	β NH, δ ring	28	a"	1002	975	975	γ CH
9	a'	1520	1489	1504	β NH, $\nu(C_6N_{10})$	29	a"	937	909	890	γ CH
10	a'	1488	1446	1438	β CH, $\nu(C_4C_5)$	30	a"	822	807	797	τ ring
11	a'	1460	1423	1435	$\nu(N_1C_2)$, $\nu(N_7C_8)$	31	a"	722	703	686	γ NH
12	a'	1456	1423	1402	β NH, δ ring	32	a"	671	644	604	γ NH
13	a'	1449	1417	1364	β CH, δ ring	33	a"	651	638	585	γ NH
14	a'	1403	1373	1342	β CH, δ ring	34	a"	616	595	572	η NH
15	a'	1333	1311	1261	β CH, δ ring	35	a"	567	552	514	γ CH, τ ring
16	a'	1229	1205	1183	β CH, δ ring	36	a"	439	428	443	γ CH, τ ring
17	a'	1213	1183	1137	δ ring, β NH	37	a"	274	269	259	τ ring, γ CH
18	a'	1135	1115	1084	β NH, β CH	38	a"	220	214	215	τ ring, γ

											CH
19	a'	1125	1096	1013	β NH, δ ring	39	a"	141	139	129	τ ring, γ NH
20	a'	1008	989	998	β NH, δ ring						

[a] CASSCF harmonic frequencies scaled by 0.91.

Figure S2: Optimized structure of singlet 3-adenine (X^1A') obtained at PBE0/aug-cc-pVDZ level. The numbering of the atoms used in the tables is also given.

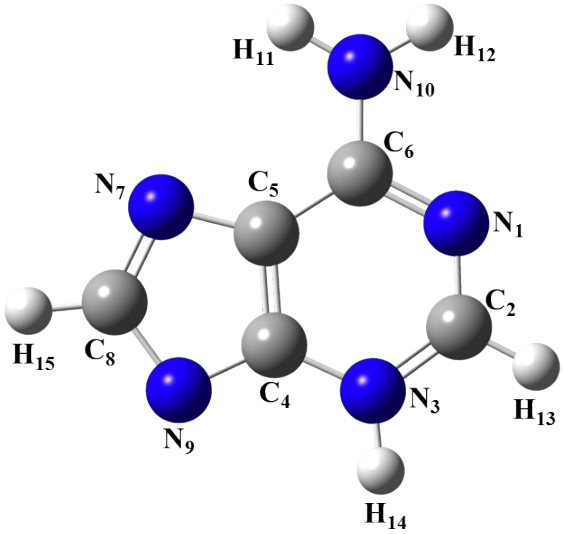

Table S7: Main geometrical parameters (Å and degrees) of the neutral and cation of 3H-adenine and 3H-adenine$^+$, obtained at PBE0/aug-cc-pVDZ level of theory.

Bonds and Angles	3H-adenine (X^1A')	3H-adenine$^+$ (X^2A'')
N_1-C_2	1.308	1.300
C_2-N_3	1.349	1.372
N_3-C_4	1.368	1.343
C_4-C_5	1.411	1.450
C_5-C_6	1.397	1.434
C_6-N_1	1.364	1.361
C_6-N_{10}	1.343	1.314
C_5-N_7	1.365	1.312
N_7-C_8	1.335	1.401
C_8-N_9	1.369	1.339
N_9-C_4	1.328	1.333
N_{10}-H_{11}	1.008	1.014
N_{10}-H_{12}	1.007	1.015
C_2-H_{13}	1.090	1.091
C_8-H_{15}	1.088	1.088
N_3-H_{14}	1.012	1.018
N_1-C_2-N_3	125.0	125.8
C_2-N_3-C_4	118.5	118.5
N_3-C_4-C_5	119.0	119.0
C_4-C_5-C_6	118.7	118.0
C_5-C_6-N_1	119.9	119.0
C_5-C_6-N_{10}	122.8	122.5
C_4-C_5-N_7	108.1	108.8
C_5-N_7-C_8	101.9	101.9
N_7-C_8-N_9	118.0	117.3
C_8-N_9-C_4	100.8	101.5

Table S8: Harmonic and anharmonic frequencies (in cm^{-1}) of 3H-adenine and of 3H-adenine$^+$ in their electronic ground states obtained at PBE0/aug-cc-pVDZ level of theory. Anharmonic frequencies are arranged according to the harmonic frequencies. (In plane vibration: ν stretching, β bending, δ deformation. Out of plane vibration: γ wagging, η twisting, τ torsion.

		3H-adenine (X^1A')					**3H-adenine (X^1A')**		
No.	Symm.	Harm.	Anharm.	Assignment	No.	Symm.	Harm.	Anharm.	Assignment
1	a'	3775	3580	ν NH	21	a'	a'	956	δ ring, β NH
2	a'	3632	3458	ν NH	22	a"	a"	932	γ CH
3	a'	3628	3449	ν NH	23	a"	a"	927	γ CH
4	a'	3247	3117	ν CH	24	a'	a'	911	δ ring
5	a'	3222	3087	ν CH	25	a"	a"	800	τ ring
6	a'	1716	1674	ν (C_5C_6), ν (C_6N_{10})	26	a'	a'	731	δ ring
7	a'	1646	1606	β NH, ν (C_4N_3)	27	a"	a"	710	γ NH
8	a'	1631	1591	β NH, δ ring	28	a"	a"	672	γ CH, γ NH
9	a'	1568	1533	β NH, ν (C_6N_{10})	29	a"	a"	662	γ NH
10	a'	1517	1482	β NH, ν (C_4C_5)	30	a'	a'	612	τ ring, β NH
11	a'	1499	1463	β NH, β CH	31	a"	a"	578	η NH
12	a'	1472	1442	β CH, δ ring	32	a"	a"	553	η NH, γ CH
13	a'	1394	1363	β CH, δ ring	33	a'	a'	527	τ ring
14	a'	1384	1358	β CH, δ ring	34	a'	a'	510	β NH, β CH
15	a'	1328	1300	β CH, δ ring	35	a"	a"	303	τ ring
16	a'	1271	1249	β CH, δ ring	36	a'	a'	274	β NH, β CH
17	a'	1210	1184	β CH, δ ring	37	a"	a"	243	γ NH
18	a'	1193	1172	β NH, β CH	38	a"	a"	195	γ NH, τ ring
19	a'	1148	1128	β NH, β CH	39	a"	a"	156	τ ring, γ CN
20	a'	1002	1009	β NH, β CH					
		3H-adenine$^+$ (X^2A'')					**3H-adenine$^+$ (X^2A'')**		
No.	Symm.	Harm.	Anharm.	Assignment	No.	Symm.	Harm.	Anharm.	Assignment
1	a'	3686	3508	ν NH	21	a"	977	955	γ CH
2	a'	3570	3394	ν NH	22	a"	949	919	γ CH

3	a'	3549	3396	ν NH	23	a'	917	902	δ ring
4	a'	3269	3141	ν CH	24	a'	862	850	δ ring
5	a'	3230	3108	ν CH	25	a"	806	793	τ ring
6	a'	1698	1659	β NH, ν (C_6N_{10})	26	a"	758	730	γ NH
7	a'	1685	1637	β NH, β *C*H	27	a'	731	722	δ ring, β NH
8	a'	1650	1610	β NH, δ ring	28	a"	709	689	γ NH
9	a'	1538	1511	β NH, δ ring	29	a"	661	643	γ NH
10	a'	1513	1463	β NH, β CH	30	a"	630	611	γ NH
11	a'	1483	1450	δ ring	31	a'	596	588	δ ring, β NH
12	a'	1458	1423	β CH, δ ring	32	a"	518	504	γ CH
13	a'	1417	1378	β CH, β NH	33	a'	513	507	δ ring, β NH
14	a'	1379	1353	β CH, β NH	34	a'	509	505	β NH, δ ring
15	a'	1299	1264	β CH, β NH	35	a"	499	489	γ CH, γ NH
16	a'	1248	1213	β CH, β NH	36	a'	278	277	τ ring, γ NH
17	a'	1178	1152	β CH, β NH	37	a"	271	267	τ ring, γ NH
18	a'	1127	1105	β CH, β NH	38	a"	212	207	τ ring, γ CH
19	a'	1032	994	N (N_7C_8), β CH	39	a"	139	137	γ NH, γ CN
20	a'	994	969	β NH					

Figure S3: Optimized structure of singlet 7-adenine (X^1A) obtained at PBE0/aug-cc-pVDZ level. The numbering of the atoms used in the tables is also given.

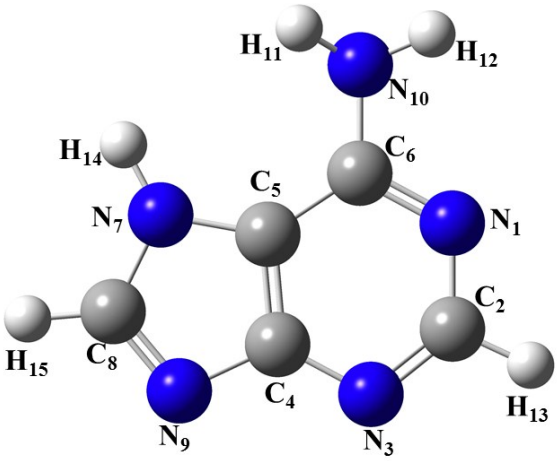

Table S9: Main geometrical parameters (Å and degrees) of the neutral and cation of 7-adenine and 7-adenine$^+$, obtained at PBE0/aug-cc-pVDZ level of theory.

Bonds and Angles	7-adenine (X^1A')	7-adenine$^+$ (X^2A'')
N_1-C_2	1.345	1.315
C_2-N_3	1.324	1.372
N_3-C_4	1.341	1.306
C_4-C_5	1.405	1.440
C_5-C_6	1.400	1.431
C_6-N_1	1.332	1.350
C_6-N_{10}	1.375	1.327
C_5-N_7	1.379	1.341
N_7-C_8	1.368	1.408
C_8-N_9	1.308	1.291
N_9-C_4	1.378	1.384
N_{10}-H_{11}	1.009	1.011
N_{10}-H_{12}	1.012	1.016
C_2-H_{13}	1.092	1.091
C_8-H_{15}	1.086	1.087
N_7-H_{14}	1.008	1.013
N_1-C_2-N_3	128.7	128.3
C_2-N_3-C_4	113.1	114.3
N_3-C_4-C_5	123.2	123.3
C_4-C_5-C_6	118.6	117.1
C_5-C_6-N_1	118.9	118.3
C_5-C_6-N_{10}	123.8	125.0
C_4-C_5-N_7	105.2	105.2
C_5-N_7-C_8	106.0	106.6
N_7-C_8-N_9	114.0	114.6
C_8-N_9-C_4	104.5	104.9

Table S10: Harmonic and anharmonic frequencies (in cm^{-1}) of 7H-adenine and of 7H-adenine$^+$ in their electronic ground states obtained at PBE0/aug-cc-pVDZ level of theory. Anharmonic frequencies are arranged according to the harmonic frequencies. (In plane vibration: ν stretching, β bending, δ deformation. Out of plane vibration: γ wagging, η twisting, τ torsion.)

		7H-adenine (X^1A')					**7H-adenine (X^1A')**		
No.	Symm.	Harm.	Anharm.	Assignment	No.	Symm.	Harm.	Anharm.	Assignment
1	a	3715	3551	ν NH	21	a	987	966	γ CH
2	a	3692	3524	ν NH	22	a	950	944	δ ring, β NH
3	a	3591	3442	ν NH	23	a	898	887	δ ring
4	a	3265	3141	ν CH	24	a	891	868	γ CH
5	a	3196	3067	ν CH	25	a	827	809	τ ring
6	a	1704	1671	ν (C_5C_6), δ ring	26	a	735	725	δ ring
7	a	1650	1611	β NH, δ ring	27	a	711	692	τ ring
8	a	1614	1580	β NH, δ ring	28	a	643	611	γ CH, γ NH
9	a	1554	1522	β CH, ν (C_8N_9)	29	a	616	608	δ ring, β NH
10	a	1527	1488	β CH, β NH	30	a	587	554	γ CH
11	a	1447	1409	β NH, ν (N_7C_8)	31	a	549	459	γ NH
12	a	1427	1394	N (C_4C_5), β CH	32	a	534	478	γ NH
13	a	1408	1376	β CH, δ ring	33	a	522	515	γ NH, δ ring
14	a	1369	1338	β CH, δ ring	34	a	437	412	γ NH
15	a	1355	1327	β CH, δ ring	35	a	347	309	γ NH
16	a	1297	1276	β CH, δ ring	36	a	303	297	γ NH
17	a	1244	1218	β CH, β NH	37	a	287	284	τ ring
18	a	1149	1124	β NH, δ ring	38	a	209	204	τ ring, γ NH
19	a	1105	1084	β NH, β CH	39	a	158	153	τ ring, γ NH
20	a	1041	1030	β NH, β CH					
		7H-adenine$^+$ (X^2A'')					**7H-adenine$^+$ (X^2A'')**		
No.	Symm.	Harm.	Anharm.	Assignment	No.	Symm.	Harm.	Anharm.	Assignment
1	a'	3703	3529	ν NH	21	a'	998	974	β NH, δ ring
2	a'	3630	3463	ν NH	22	a"	927	904	γ CH
3	a'	3551	3397	ν NH	23	a'	913	902	δ ring
4	a'	3272	3152	ν CH	24	a'	883	868	δ ring
5	a'	3230	3100	ν CH	25	a"	806	791	τ ring

6	a'	1688	1640	β NH, δ ring	26	a'	741	717	δ ring
7	a'	1667	1625	β NH, δ ring	27	a"	722	705	γ NH, τ ring
8	a'	1623	1586	β NH, ν (C_4N_3)	28	a"	646	628	γ NH, γ CH
9	a'	1556	1512	β NH, ν (C_8N_9)	29	a"	614	591	γ NH, γ CH
10	a'	1499	1459	β CH, β NH	30	a'	596	589	β NH, δ ring
11	a'	1471	1429	β NH, β CH	31	a"	578	559	γ NH, γ CH
12	a'	1423	1392	β CH, δ ring	32	a"	534	514	γ NH
13	a'	1394	1367	β NH, δ ring	33	a'	534	526	β NH, δ ring
14	a'	1365	1332	β CH, β NH	34	a'	491	486	δ ring, β NH
15	a'	1352	1319	β CH, δ ring	35	a"	385	367	γ CH
16	a'	1266	1245	β CH, β NH	36	a'	300	297	β NH, β CH
17	a'	1210	1187	β NH, δ ring	37	a"	265	262	δ ring, γ NH
18	a'	1104	1080	β CH, δ ring	38	a"	214	210	δ ring, γ CH
19	a'	1023	991	β NH, β CH	39	a"	123	127	δ ring, γ NH
20	a"	1002	975	γ CH					

Table S11: Total energies (in Hartrees) and adiabatic ionization energy (in eV) of the 9H-adenine$^+$($1^2A'$) at the (R)CCSD(T)-F12(b)/cc-pVTZ-F12 (+CV+SR+ZPVE) level. ZPVE corresponds to the zero point vibrational energy (in cm^{-1}).

	9H-adenine ($\widetilde{X}^2A''$)	9H-adenine$^+$ ($1^2A'$)
Total energies		
PBE0/aug-cc-pVDZ	-466.87444	-466.55207
ZPVE	24738	24766
CCSD(T)-F12b/cc-pVTZ-f12	-466.73389	-466.40063
CCSD(T,fc)/cc-pwCVTZ	-466.57363	-466.24706
CCSD(T,full)/cc-pwCVTZ	-467.07047	-466.74373
CCSD(T)/cc-pVTZ	-466.54498	-466.21870
CCSD(T)/cc-pVTZ-DK	-466.76288	-466.43664
Adiabatic ionization energy		
CCSD(T)-F12b	9.069	
CV	0.004	
SR	-0.001	
ZPVE	0.003	
IE(F12b+CV+SR+ZPVE)	9.075	