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

Supplementary material

Threshold photoelectron spectroscopy of 9-methyladenine: theory and experiment

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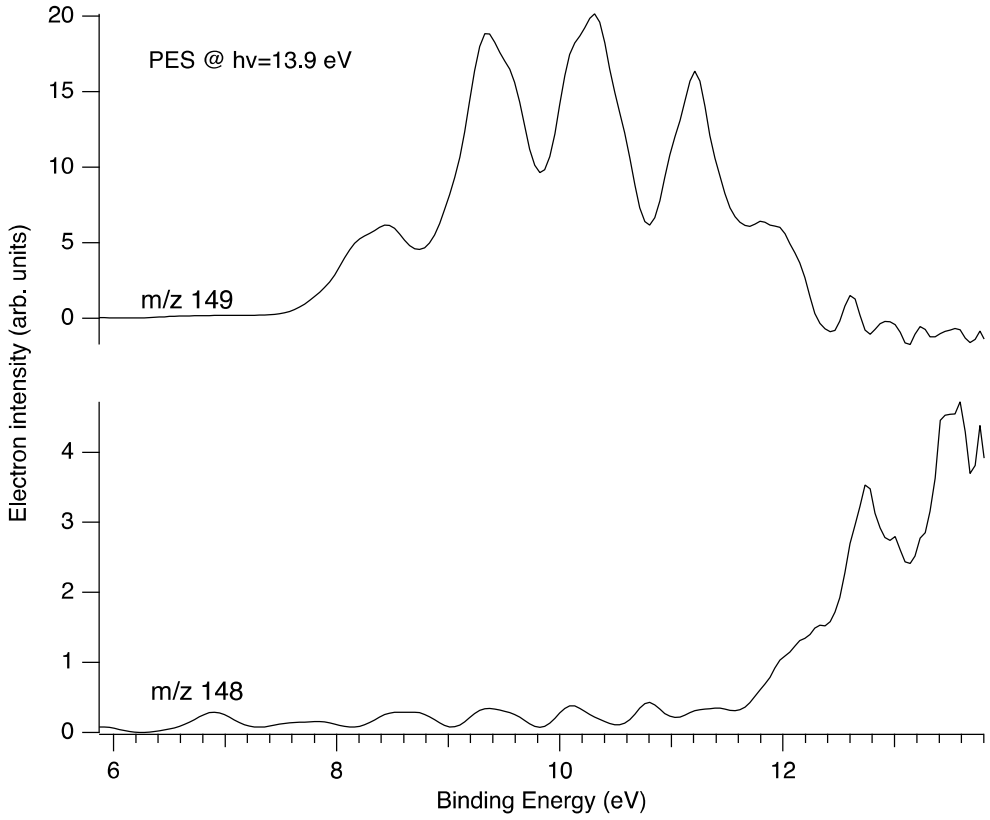


Figure S1: PES spectrum of 9MA obtained for hν = 13.9 eV. We give also that of the m/z = 148 H loss fragment.

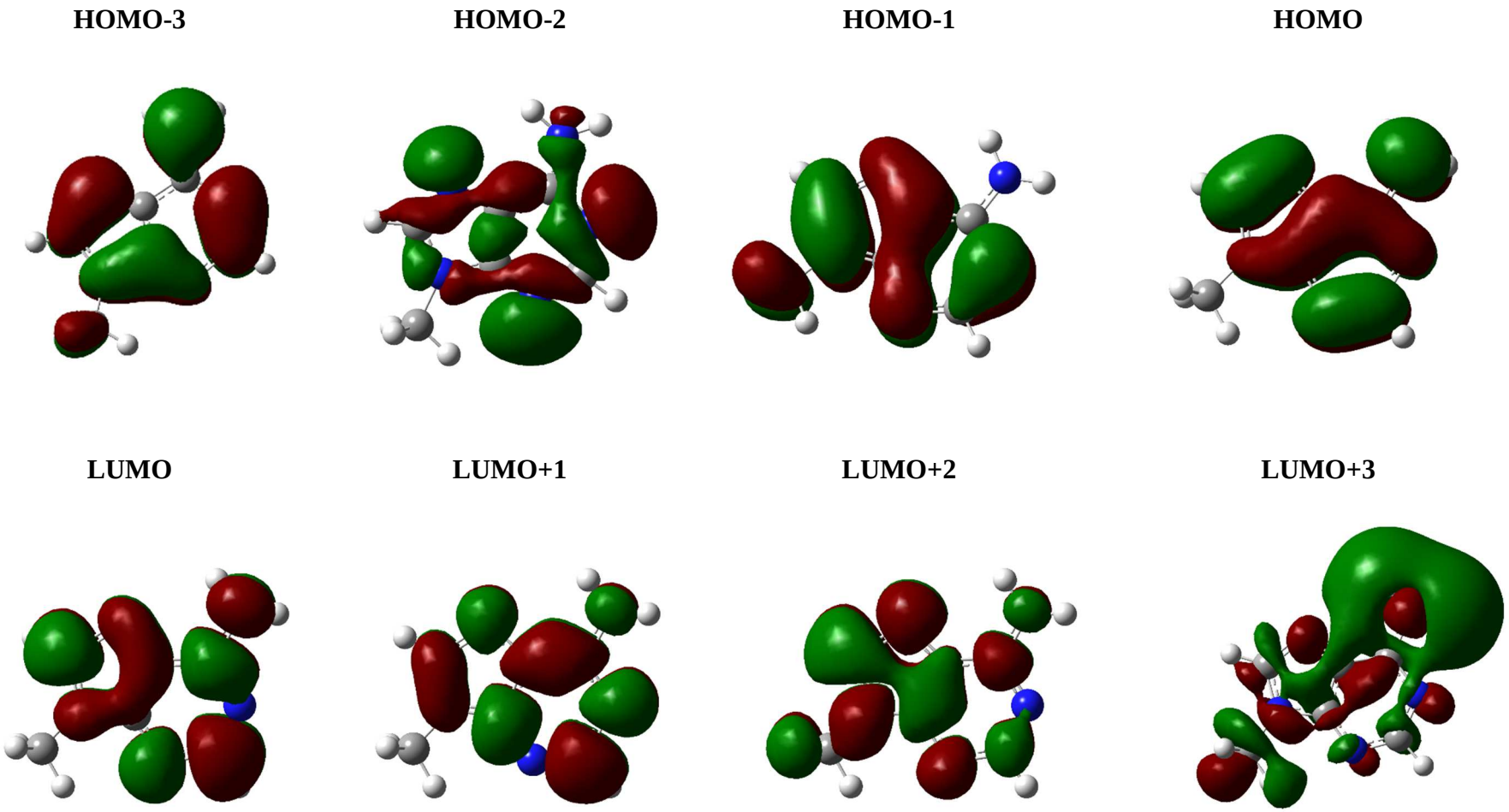


Figure S2: Outermost molecular orbitals of 9MA.

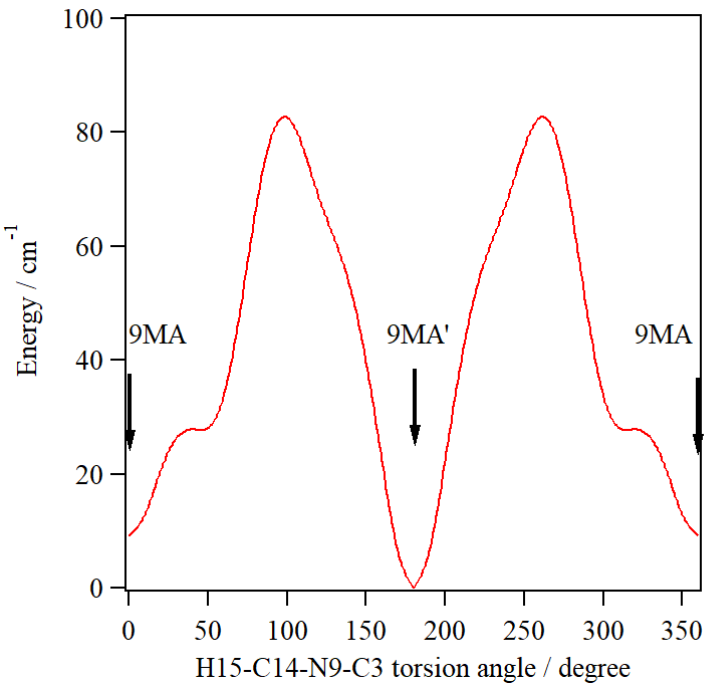
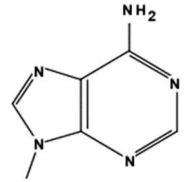
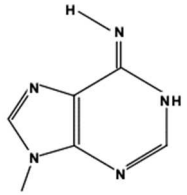
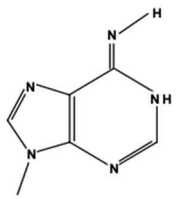
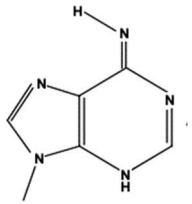
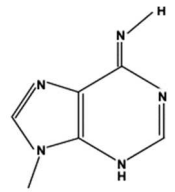


Figure S3: PBE0/auc-cc-pVDZ one dimensional cut of the potential energy surface of 9-methyladenine by rotating the methyl group along the N9-C3 bond. The black arrows locate the 9MA′ and 9MA species.

Table S1: Total energies (in Hartree) and adiabatic ionization energies (AIE in eV) of 9-methyladenine (9MA) and of its conformer (9MA′) and tautomers as computed at the PBE0/aug-cc-pVDZ level and (R)CCSD(T)-F12/aug-cc-pVDZ level of theory. ZPVE (in Hartree) corresponds to the zero-point vibrational energy (in Hartree) as computed at the anharmonic level of theory. The equilibrium geometries in Cartesian coordinates are given in Table S2.

Molecular species											
	9MA	9MA′	$9MA^+$	I1(1H)	$I1(1H)^+$	I2(1H)	$I2(1H)^+$	I1(3H)	$I1(3H)^+$	I2(3H)	$I2(3H)^+$
Method	Total energies (in Hartree)										
PBE0 / aug-cc-pVDZ (optg) [(a)]	-506.138191	-506.138150	-505.849182	-506.119026	-505.842185	-506.108655	-505.832716	-506.088016	-505.814529	-506.087799	-505.816232
ZPVE [(a)]	0.140330	0.140281	0.140783	0.141482	0.140527	0.140898	0.140072	0.140199	0.139360	0.140064	0.139410
(R)CCSD(T)-F12 / aug-cc-pVDZ (SP) [(b)]	-505.882538	-505.882723	-505.586090	-505.863762	-505.578837	-505.853478	-505.552047	-505.834044	-505.552712	-505.833628	-505.551991

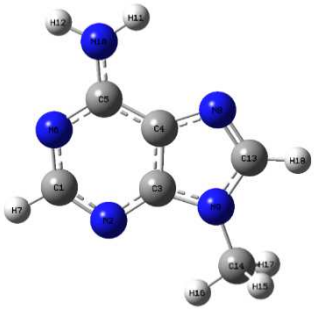
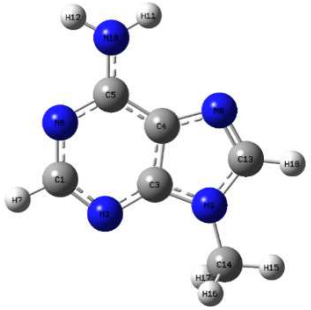
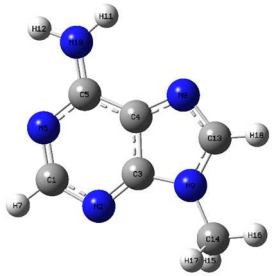
[(a)] optg stands for full optimization computations.
[(b)] SP is for single point computations as the optimized PBE0/aug-cc-pVDZ geometry.

Table S2: Optimized geometries of 9-methyladenine in Cartesian coordinated as computed at the PBE0/au-cc-pVDZ level of theory.

9MA	**9MA′**	**9MA$^+$**	
C -1.06279700 1.93691600 0.00095700	C 1.10276500 1.92235900 0.00003100	C 0.558695 0.444630 -0.000000	
N 0.25389900 1.73825900 -0.00024700	N -0.25710900 1.71004600 -0.00022900	C -0.359508 -0.649611 -0.000000	
C 0.54513100 0.43380700 -0.00069400	C -0.55871500 0.44457500 -0.00006500	C -1.744755 -0.280951 0.000000	
C -0.36182500 -0.62724300 -0.00081900	C 0.35956900 -0.64968400 0.00014400	C -1.102807 1.922433 0.000000	
C -1.72375400 -0.26967400 -0.00076900	C 1.74486000 -0.28087800 0.00011000	N 0.257046 1.710117 -0.000000	
N -2.04993000 1.03088800 0.00117700	N 2.07073000 1.03257300 0.00006100	N -2.070767 1.032482 0.000000	
H -1.38870800 2.97882700 0.00229600	H 1.40400200 2.97041500 -0.00005500	N 0.273036 -1.822428 0.000000	
N 0.29127200 -1.84031600 0.00051800	N -0.27297700 -1.82247700 -0.00010600	N 1.808178 -0.152983 -0.000000	
N 1.78511700 -0.15487300 0.00007300	N -1.80824000 -0.15308600 -0.00032300	C 1.578960 -1.478408 -0.000000	
N -2.71094800 -1.18983100 -0.00964200	N 2.71387300 -1.17744700 0.00003500	H -1.404212 2.970454 0.000000	
H -2.48753300 -2.17035900 0.02838700	H 2.50704400 -2.16981500 0.00002400	N -2.713724 -1.177589 0.000000	
H -3.66816200 -0.88073900 0.02827000	H 3.67873400 -0.86268000 -0.00002800	H -3.678575 -0.862812 0.000000	
C 1.56020500 -1.50946600 0.00087600	C -1.57900500 -1.47841700 0.00000600	H -2.506965 -2.169976 0.000000	
C 3.05337000 0.53818900 -0.00014800	C -3.08818400 0.54209300 0.00025100	H 2.389263 -2.203359 -0.000000	
H 3.63296800 0.28832600 -0.89761400	H -3.16189100 1.16959600 -0.89434000	C 3.088060 0.541998 0.000000	
H 2.84148600 1.61205200 0.00324800	H -3.88976000 -0.20153300 0.00098100	H 3.161401 1.170112 -0.894680	
H 3.63585200 0.28314800 0.89396600	H -3.16068800 1.17004100 0.89463000	H 3.161401 1.170112 0.894680	
H 2.38623800 -2.21531600 0.00187400	H -2.38912900 -2.20358000 -0.00014700	H 3.889450 -0.201788 0.000000	
I1(1H)	**I1(1H)$^+$**	**I2(1H)**	**I2(1H)$^+$**
C -3.01110800 0.64640500 0.00035400	C -3.04628200 0.63552900 0.00015000	C -3.01099600 0.65402700 -0.00015300	C -3.04836700 0.63457300 -0.00016000
H -2.74893800 1.70873400 -0.00053300	H -2.81109300 1.70331600 -0.00076400	H -2.74313500 1.71506500 -0.00112500	H -2.81297400 1.70228300 -0.00111200
N -1.77959000 -0.11188900 0.00001600	N -1.78673700 -0.10041800 0.00005500	N -1.78510300 -0.11195900 -0.00009500	N -1.79013700 -0.10255300 -0.00007900
C -1.62873900 -1.47420100 0.00001700	C -1.61473600 -1.46069800 0.00023300	C -1.64047600 -1.47527300 0.00011700	C -1.61797200 -1.46463400 0.00012400
H -2.48701700 -2.13934600 0.00009300	H -2.46497900 -2.13855300 0.00020700	H -2.50278700 -2.13571700 0.00015800	H -2.46881500 -2.14199800 0.00016600
N -0.37203200 -1.85879200 -0.00055100	N -0.34687600 -1.85416200 -0.00027000	N -0.38782700 -1.86752500 0.00020800	N -0.35104500 -1.85973900 0.00021800
C 0.33852300 -0.68930800 0.00005100	C 0.34589100 -0.70424600 0.00000100	C 0.33322900 -0.70426600 0.00010400	C 0.34520000 -0.71414000 0.00010600
C 1.76571500 -0.47298400 0.00040100	C 1.74928500 -0.45374300 0.00002100	C 1.76361300 -0.49128800 0.00014200	C 1.75473200 -0.46321700 0.00013500
N 2.76655100 -1.27155800 0.00021400	N 2.76207900 -1.26741900 -0.00010900	N 2.66641700 -1.39810700 0.00030400	N 2.64270800 -1.40520600 0.00029800
N 2.02808500 0.91471600 0.00011700	N 2.03970400 0.91726500 -0.00003000	H 3.60641700 -0.99899700 0.00029500	H 3.60786300 -1.06167800 0.00029300
C 1.10080800 1.90522400 -0.00023300	C 1.12779700 1.89502500 -0.00002300	N 2.02114000 0.90764200 -0.00003000	N 2.03471600 0.91953800 -0.00003900
H 1.50142300 2.91948300 -0.00026400	H 1.50836900 2.91612400 -0.00005000	C 1.08992000 1.90224300 -0.00021400	C 1.11237600 1.89479500 -0.00021600
N -0.18787500 1.73027300 -0.00026300	N -0.18586500 1.70504100 -0.00000600	H 1.49066400 2.91700100 -0.00034000	H 1.49024100 2.91744700 -0.00034400
C -0.51281500 0.40608500 -0.00023100	C -0.53524800 0.42741300 -0.00002200	N -0.19382400 1.72215600 -0.00025000	N -0.19605000 1.70110800 -0.00024600
H -3.60250000 0.42166100 0.89644500	H -3.62066100 0.38602100 0.89862500	C -0.51554700 0.39635000 -0.00008000	C -0.53972400 0.42041500 -0.00008300

H -3.60364700 0.42043000 -0.89466100	H -3.62154800 0.38468100 -0.89737800	H -3.60442800 0.43293400 0.89578600	H -3.62316300 0.38497800 0.89808100
H 3.01138800 1.15605200 0.00019600	H 3.03045400 1.15172900 -0.00008200	H -3.60519700 0.43146200 -0.89520800	H -3.62385200 0.38352800 -0.89755100
H 2.42902000 -2.23357400 -0.00015700	H 2.44308000 -2.24113700 -0.00021000	H 2.99438600 1.18205600 -0.00002000	H 3.01188700 1.19665200 -0.00003300
I1(3H)	**I1(3H)$^+$**	**I2(3H)**	**I2(3H)$^+$**
N -1.76736300 -0.12679600 -0.00002100	N -1.76613500 -0.12187600 -0.00002600	N 1.77687100 -0.12133300 -0.00002800	N 1.77438300 -0.11601700 0.00001800
C -1.59399700 -1.49700100 0.00029600	C -1.56390000 -1.49538100 -0.00034400	C 1.62226500 -1.49426800 0.00052400	C 1.58753900 -1.49393400 0.00005100
H -2.44926100 -2.16577300 0.00043700	H -2.40990500 -2.17825900 -0.00033000	H 2.48731800 -2.15075700 0.00071000	H 2.44226200 -2.16619400 0.00002500
N -0.33587500 -1.85315600 0.00003200	N -0.30225300 -1.85226400 0.00021800	N 0.37150300 -1.87057800 -0.00065700	N 0.33152900 -1.86777300 -0.00013100
C 0.37172200 -0.67454600 -0.00008800	C 0.38622400 -0.68278000 0.00007900	C -0.35717800 -0.70432200 -0.00002000	C -0.37344100 -0.71006600 -0.00001800
C 1.81184600 -0.43853100 -0.00032600	C 1.78339000 -0.40166900 0.00020900	C -1.79632800 -0.46657600 0.00004700	C -1.77198700 -0.42553000 -0.00002000
N 2.74444700 -1.31637200 -0.00004100	N 2.74878800 -1.30936100 0.00024800	N -2.66684100 -1.40410400 -0.00038000	N -2.65440300 -1.40629400 -0.00012600
H 2.31426200 -2.24449900 0.00022200	H 2.33186900 -2.24949600 0.00022800	H -3.59528400 -0.97583500 -0.00042700	H -3.59935100 -1.00225800 -0.00014300
N 2.17097700 0.93081800 -0.00002300	N 2.16576900 0.92491300 -0.00000700	N -2.16199800 0.90703700 0.00018000	N -2.15965000 0.90482600 0.00001300
C 1.28866600 1.85885300 0.00014200	C 1.28824200 1.86779300 -0.00018700	C -1.28549400 1.84331300 0.00029300	C -1.28769900 1.85314800 0.00006800
H 1.60612700 2.90482800 0.00016700	H 1.59979900 2.91286900 -0.00024000	H -1.60954200 2.88716100 0.00038000	H -1.60353500 2.89686700 0.00009700
N -0.08279600 1.68819500 0.00008100	N -0.08330600 1.66785700 -0.00018400	N 0.07993000 1.67257600 0.00019900	N 0.08165700 1.65421200 0.00007700
C -0.50486100 0.38522100 0.00005100	C -0.52582000 0.40452600 -0.00010300	C 0.50677900 0.36908500 0.00009000	C 0.52867900 0.39177600 0.00003200
H -0.70599400 2.48058200 0.00012500	H -0.70803100 2.46915100 -0.00026000	H 0.70338000 2.46485700 0.00022500	H 0.70566400 2.45591200 0.00011300
C -3.01226400 0.60269000 -0.00016800	C -3.04164900 0.58146000 0.00009700	C 3.00918500 0.62805300 -0.00018300	C 3.03984200 0.60392200 0.00002700
H -3.09985600 1.23093300 0.89692200	H -3.13434300 1.19918700 0.90160400	H 3.08837100 1.25733900 -0.89756700	H 3.12551500 1.22284800 -0.90148700
H -3.09985800 1.23067100 -0.89744400	H -3.13431900 1.19938700 -0.90127100	H 3.08825800 1.25766700 0.89697200	H 3.12549200 1.22283500 0.90155200
H -3.83782100 -0.11568100 -0.00006200	H -3.84403700 -0.16142200 0.00000500	H 3.84586700 -0.07732600 0.00000400	H 3.85174000 -0.12858200 0.00003300

Table S3: PBE0/aug-cc-pVDZ main geometrical parameters (distances in Å and angles in degrees) of 9MA, of 9MA′ and of $9MA^+$ in their respective electronic ground state.

	9MA 				**9MA′** 	**$9MA^+$** 	
Coordinate	This work	HF/4-21G [a]	B3LYP/6-31G* [b]	MP2/ 6-31G* [c]	This work	This work	M06-2X/6-31+G(d,p) [d]
$C_1 - N_2$	1.332	1.325	1.336	1.339	1.332	1.376	1.381
$N_2 - C_3$	1.337	1.336	1.339	1.344	1.337	1.301	1.297
$C_3 - C_4$	1.396	1.382	1.399	1.398	1.396	1.429	1.430
$C_4 - C_5$	1.408	1.396	1.410	1.410	1.408	1.434	1.436
$C_5 - N_6$	1.341	1.337	1.345	1.343	1.341	1.353	1.357
$N_6 - C_1$	1.340	1.339	1.343	1.353	1.340	1.315	1.312
$C_3 - N_9$	1.373	1.366	1.380	1.377	1.372	1.385	1.389
$N_9 - C_{13}$	1.373	1.388	1.381	1.372	1.373	1.345	1.342
$C_{13} - N_8$	1.311	1.295	1.312	1.328	1.311	1.351	1.353
$N_8 - C_4$	1.378	1.398	1.384	1.378	1.378	1.333	1.328
$N_9 - C_{14}$	1.445	1.459	1.454	1.451	1.444	1.457	1.465
$C_5 - N_{10}$	1.350	1.341	1.358	1.353	1.350	1.320	1.317
$C_1 - H_7$	1.092	1.068	1.088	/	1.092	1.091	/
$N_{10} - H_{11}$	1.006	0.996	1.009	/	1.006	1.014	/
$N_{10} - H_{12}$	1.007	0.996	1.009	/	1.007	1.015	/
$C_{13} - H_{18}$	1.087	1.065	1.083	/	1.087	1.087	/
$C_{14} - H_{15}$	1.097	1.081	1.095	/	1.095	1.095	/
$C_{14} - H_{16}$	1.095	1.080	1.091	/	1.097	1.093	/
$C_{14} - H_{17}$	1.097	1.081	1.095	/	1.097	1.095	/

$N_6{-}C_1{-}N_2$	128.9	126.57	128.6	129.0	128.9	128.5	
$C_1 - N_2 - C_3$	111.2	113.23	111.2	110.6	111.1	112.3	
$N_2{-}C_3{-}C_4$	126.9	125.26	127.0	127.3	126.9	126.6	
$C_3 - C_4{-}C_5$	115.8	117.16	115.8	115.6	115.8	115.1	
$C_4{-}C_5 - N_6$	118.8	117.97	118.9	119.0	118.8	118.8	
$C_5 - N_6{-}C_1$	118.5	119.78	118.3	118.3	118.5	118.6	
$C_4 - C_5{-}N_{10}$	122.3	122.73	122.3	121.9	122.3	122.3	
$C_3 - C_4 - N_8$	111.2	109.85	111.3	111.9	111.2	111.6	
$C_4 - N_8 - C_{13}$	103.7	104.97	103.7	102.9	103.6	103.6	
$N_8 - C_{13} - N_9$	114.0	112.87	114.2	114.2	114.1	114.5	
$C_{13} - N_9 - C_3$	105.9	106.16	105.8	106.1	105.9	105.8	
$N_9 - C_3 - N_2$	127.9	128.6	127.9	127.8	127.9	128.9	
$N_6{-}C_1 - H_7$	115.2	116.27	115.2		115.2	116.5	
$C_{13} - N_9 - C_{14}$	128.1	128.18	128.3	128.2	128.0	128.3	
$N_8{-}C_{13} - H_{18}$	124.9	125.8	124.9		120.9	123.4	
$C_5 - N_{10} - H_{12}$	119.1	118.94	117.8		119.1	119.2	
$C_5 - N_{10} - H_{11}$	120.1	120.72	119.0		120.1	121.0	
$H_{12} - N_{10} - H_{11}$	120.6	120.35	119.0		120.6	119.8	
$N_9 - C_{14}{-}H_{15}$	110.8	110.06	110.8		108.8	109.4	
$N_9 - C_{14}{-}H_{16}$	107.5	108.83	107.5		110.3	108.6	
$N_9 - C_{14}{-}H_{17}$	110.7	110.06	110.8		110.3	109.4	

a. Ref. [1].
b. Ref. [2].
c. Ref. [3].
d. Ref. [4].

Table S4: Total energies (in Hartree) and adiabatic ionization energies (AIE in eV) of 9-methyladenine (9MA) and of its conformer (9MA′) at the (R)CCSD(T)-F12/aug-cc-pVDZ (+ΔCV+ΔSR+ΔZPVE) level of theory. ΔZPVE corresponds to the zero-point vibrational energy (in Hartree) as computed at the anharmonic level of theory.

Molecular species	9MA	9MA′	$9MA^+$
Total energies (in Hartree)			
PBE0/aug-cc-pVDZ (optg) [(a)]	-506.138191	-506.138150	-505.849182
ZPVE	0.140330	0.140281	0.140783
(R)CCSD(T)-F12/aug-cc-pVDZ (SP)[(b)]	-505.882538	-505.882723	-505.586090
CCSD(T,fc)/cc-pwCVTZ (SP)[(b)]	-505.811989	-505.812060	-505.520508
CCSD(T,full)/cc-pwCVTZ (SP)[(b)]	-506.357299	-506.357359	-506.06517
CCSD(T)/cc-pVTZ (SP)[(b)]	-505.781274	-505.781335	-505.490057
CCSD(T)/cc-pVTZ-DK (SP)[(b)]	-505.766344	-505.766406	-505.475134
Ionization energies (in eV)			
PBE0+ZPVE (optg)	7.876	7.876	
(R)CCSD(T)-F12	8.067	8.072	
ΔCV	0.01763	0.01733	
ΔSR	-0.00019	-0.00016	
ΔZPVE	0.01232	0.01366	
PBE0/aug-cc-pVDZ +ΔZPVE (optg) // (R)CCSD(T)-F12(+ΔCV+ΔSR) (SP)	8.097	8.102	

[(a)] optg stands for full optimization computations.
[(b)] SP is for single point computations as the optimized PBE0/aug-cc-pvdz geometry.

Table S5: PBE0/aug-cc-pVDZ harmonic (ω in cm^{-1}) and anharmonic frequencies (ν in cm^{-1}) of the two conformers of 9-methyadenine neutral.

9MA		9MA′	
ω	ν	ω	ν
3781	3803	3781	3918
3638	3634	3638	3723
3260	3135	3260	3134
3194	3063	3194	3059
3180	3040	3177	3032
3146	3006	3153	3006
3065	2958	3071	2957
1692	1721	1692	1742
1661	1611	1661	1606
1621	1583	1621	1578
1566	1505	1564	1508
1521	1479	1521	1468
1492	1453	1492	1475
1479	1440	1486	1461
1472	1429	1453	1393
1433	1406	1434	1378
1423	1392	1420	1420
1393	1353	1395	1356
1381	1367	1385	1364
1370	1337	1371	1336
1290	1241	1288	1219
1263	1245	1269	1249
1231	1195	1231	1188
1140	1128	1140	1115
1090	1052	1085	1057
1064	1043	1062	1021
1009	872	1009	815
985	960	985	959
911	902	912	904

864	840	863	834
822	804	821	801
756	750	757	751
741	731	739	729
696	693	697	699
666	660	664	661
590	480	589	404
571	559	572	557
549	824	549	-*
539	538	542	536
530	532	529	529
312	352	311	358
306	308	304	304
248	250	257	222
221	199	215	190
199	125	195	86
115	36	113	5
54	-*	49	-*
46	-*	38	-*

* Strongly anharmonic.

Table S6: Cartesian coordinates (in Å) of the equilibrium geometries of D_0-D_4 of 9-methyladenine cation as computed at the CASSCF/aug-cc-pVDZ level.

state	Cartesian coordinates	state	Cartesian coordinates
D_0	C 0.5504654764 0.3898769628 0.00000000	D_1	C 0.5532803546 0.4175289653 -0.0052136345
	C -0.3299177446 -0.6398040612 0.00000000		C -0.3622520833 -0.6438614308 -0.0081830020
	C -1.7094058445 -0.3080866816 0.00000000		C -1.7226618023 -0.3326675362 -0.0314804785
	C -1.1437142998 1.9611516771 0.00000000		C -1.0175762322 1.9793824321 -0.0038212955
	N 0.2247402361 1.7363884936 0.00000000		N 0.2537902546 1.7613050734 -0.0338639506
	N -2.0880961807 1.0519823758 0.00000000		N -1.9862287403 0.9897759614 0.1923689496
	N 0.3188989329 -1.8381772665 0.00000000		N 0.3131996497 -1.8447404927 0.0123091320
	N 1.7792593083 -0.1575349960 0.00000000		N 1.7622347114 -0.1325612486 -0.0025563975
	C 1.5699050373 -1.5092280984 0.00000000		C 1.5468786006 -1.5069481130 0.0099877620
	H -1.4436544866 2.9930171282 0.00000000		H -1.4004746559 2.9829370951 -0.0495323060
	N -2.6726067955 -1.1590626403 -0.00000000		N -2.7206620302 -1.1867455326 -0.1550532134
	H -3.6219218050 -0.8407766790 -0.00000000		H -3.6645299476 -0.8790282340 -0.0703962270
	H -2.4800904157 -2.1420686498 -0.00000000		H -2.5333808789 -2.1630142404 -0.2289280074
	H 2.3907881986 -2.2011563366 0.00000000		H 2.3769537205 -2.1898313471 0.0145864883
	C 3.0705728703 0.5352876005 0.00000000		C 3.0584360592 0.5572061018 0.0144536862
	H 3.1576200000 1.1509200000 -0.8872223		H 3.0808695828 1.3025028400 -0.7698169969
	H 3.1576200000 1.1509200000 0.8872223		H 3.2127267704 1.0279642103 0.9778528007
	H 3.8537937275 -0.2114307778 0.00000000		H 3.8335566669 -0.1772575042 -0.1621303094
D_2	C 0.5439619855 0.4261106126 0.0002634523	D_4	C 0.5765608359 0.4173499331 -0.0097790370
	C -0.3607335962 -0.6346116629 0.0000896471		C -0.3621619921 -0.6226398441 -0.0353548899
	C -1.7345748573 -0.3343445168 0.0032748475		C -1.7316953980 -0.3079782112 -0.0455102379
	C -1.0228804761 2.0089336213 -0.0042227801		C -1.1042448314 1.9795930099 -0.0034296159
	N 0.2483214104 1.7600975091 -0.0037318890		N 0.2773113904 1.7613503794 0.0060804233
	N -1.9568647732 0.9947704403 0.0347380205		N -2.0878197461 1.0178694658 -0.0282332700
	N 0.3039785990 -1.8332115922 0.0019380465		N 0.2845565295 -1.8272329004 -0.0467123103
	N 1.7671609293 -0.1392589771 -0.0006753299		N 1.7873711271 -0.1414036080 -0.0075136291
	C 1.5464124592 -1.4936552152 0.0014289487		C 1.5730564324 -1.5043734011 -0.0277829661
	H -1.4044471498 3.0125911877 -0.0143611198		H -1.4280117248 3.0021988714 0.0134479031
	N -2.7250830162 -1.2046370621 -0.0045483127		N -2.7082176070 -1.1958608972 -0.0683718435
	H -3.6772304394 -0.9126616533 -0.0008557610		H -3.6566669495 -0.8883470989 -0.0797103926
	H -2.5159458125 -2.1795887629 -0.0127356776		H -2.5110706719 -2.1728634365 -0.0886307945
	H 2.3683589714 -2.1861889900 0.0022042002		H 2.3798703165 -2.2105290156 -0.0319756340
	C 3.0607179458 0.5489393376 -0.0006445893		C 3.0848162419 0.5440968867 0.0339234849
	H 3.1510318314 1.1642140093 -0.8874273698		H 3.1213423248 1.2956566925 -0.7442304691
	H 3.1499526760 1.1647374951 0.8859625669		H 3.2289502893 1.0060176532 1.0030005033
	H 3.8420233128 -0.2002887805 -0.0001139003		H 3.8602134331 -0.1909574791 -0.1386342246

Table S7: PBE0/aug-cc-pVDZ harmonic (ω in cm^{-1}) and anharmonic frequencies (ν in cm^{-1}) of the 9-methyladenine cation, $9MA^+$. In plane vibrations: ν stretching, δ deformation, β bending. Out-of-plane vibrations: η twisting, γwagging, τ torsion.

Mode	Sym	ω	ν	Assignment
1	a'	3688	3506	νNH_2 a
2	a'	3550	3389	νNH_2 s
3	a'	3272	3141	$\nu C_{13}-H_{18}$
4	a'	3229	3103	νC_1-H_7
5	a'	3205	3060	νCH_3
6	a'	3089	2973	νCH_3
7	a'	1680	1640	$\beta\ NH_2$, νC_5-N_{10}
8	a'	1670	1628	$\beta\ NH_2$,νN_2-C_3
9	a'	1612	1575	$\beta\ NH_2$,νC_5-C_4
10	a'	1555	1516	$\beta\ NH_2$, $\beta\ C_{13}-H_{18}$, νN_9-C_{13}
11	a'	1514	1485	$\beta\ NH_2$, $\beta\ C_1-H_7$
12	a'	1485	1444	$\beta\ CH_3$
13	a'	1461	1424	$\beta\ CH_3$, νN_6-C_1
14	a'	1456	1424	$\beta\ C_1-H_7$,$\beta\ C_{13}-H_{18}$, δ ring
15	a'	1429	1392	βCH_3
16	a'	1401	1372	$\beta\ C_1-H_7$
17	a'	1386	1351	$\beta\ C_{13}-H_{18}$, $\beta\ CH_3$
18	a'	1331	1308	$\beta\ C_1-H_7$,$\beta\ C_{13}-H_{18}$, $\beta\ NH_2$
19	a'	1266	1228	$\beta\ C_1-H_7$,$\beta\ C_{13}-H_{18}$, $\beta\ NH_2$
20	a'	1220	1189	$\beta\ CH_3$, $\beta\ C_{13}-H_{18}$
21	a'	1190	1164	$\beta\ NH_2$,$\beta\ C_1-H_7$,$\beta\ C_{13}-H_{18}$
22	a'	1077	1054	ηCH_3
23	a'	1047	1027	βNH_2, δ ring
24	a'	1005	986	βNH_2
25	a'	883	867	δ ring
26	a'	753	743	δ ring
27	a'	726	714	δ ring
28	a'	586	582	βNH_2, δ ring
29	a'	537	525	δ ring,βCH_2,$\beta C_{13}-H_{18}$
30	a'	504	499	δ ring
31	a'	312	313	βNH_2, βCH_3
32	a'	216	215	βCH_3, βNH_2
33	a''	3186	3044	νCH_3
34	a''	821	808	τring
35	a''	718	715	ηNH_2
36	a''	638	626	γNH_2
37	a''	620	579	ηNH_2
38	a''	573	556	δring, ηCH_2, $\gamma C_{13}-H_{18}$
39	a''	1451	1414	τCH_3

40	a''	1140	1110	$\eta\ CH_3$
41	a''	1000	973	$\eta C_1 - H_7$
42	a''	934	903	$\eta C_{13} - H_{18}$
43	a''	445	433	$\eta C_1 - N_7$,ηNH_2
44	a''	297	292	τ ring, τCH_3
45	a''	249	245	τ ring
46	a''	182	179	τ ring, τCH_3
47	a''	109	100	$\gamma NH_2, \gamma CH_3$
48	a''	74	18	τCH_3

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