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Electronic Supplementary Information
Electron ionization of the nucleobases adenine and hypoxanthine near the threshold: A combined experimental and theoretical study

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Table S1. Appearance energies (AEs) for other minor cations produced upon electron impact ionization of adenine. Fragment assignments are made based on refs. [1, 2].

Cation	Mass (*m/z*)	Experimental AE (eV)
$C_4H_3N_4^+$ / $C_5H_5N_3^+$	107	13.94 ± 0.3
$C_3H_2N_3^+$	80	15.12 ± 0.5
$C_2H_4N_3^+$	70	14.89 ± 0.2
$C_3H_3N_2^+$ / $C_2HN_3^+$	67	15.59 ± 0.3
$C_3H_2N_2^+$ / $C_2N_3^+$	66	14.16 ± 0.3
$C_3HN_2^+$	65	17.88 ± 0.4
NH_2CNH^+ / $C_2H_5N^+$	43	14.01 ± 0.3
NCN^+	40	15.67 ± 0.3 18.52 ± 0.4
$HCCN^+$	39	18.13 ± 0.2
NH_2CH^+	29	15.15 ± 0.15
HCN^+	27	13.48 ± 0.2

Table S2. Appearance energies (AEs) for other minor cations produced upon electron impact ionization of hypoxanthine. Fragment assignments are made based on ref.[3].

Cation	Mass (*m/z*)	Experimental AE (eV)
$^{13}C_5H_4N_4O^+$	137	8.80 ± 0.5
$C_4H_3N_3O^+$	109	12.34 ± 0.3
$C_3H_2N_2O^+$	82	12.61 ± 0.3
$C_3H_2N_3^+$	80	14.35 ± 0.5

Table S3. Absolute energies and zero-point corrected energies (ZPE) for the most stable cations and neutral conformers from adenine calculated using B3LYP/6-311+G(2d,p).

Cation	Mass (*m/z*)	Absolute energy (h)	Zero-Point corrected energy (h)
$C_5H_5N_5^+$	135	-467.1663893	-467.054801
$C_4H_4N_4^+$	108	-373.5429667	-373.460192
$C_3H_3N_3^+$	81	-280.0703798	-280.007429
$C_2H_2N_2^+$	54	-186.5514422	-186.515235
$C_2HN_2^+$	53	-185.9467569	-185.921894
$HCNH^+$	28	-93.73493916	-93.709041
Neutral fragment	Mass (*m/z*)	Absolute energy (h)	Zero-Point corrected energy (h)
$C_4H_3N_4$	107	-373.1807003	-373.109067
$C_3H_4N_3$	82	-281.0271762	-280.953091
$C_3H_3N_3$	81	-280.3794029	-280.318791
$C_2H_2N_2$	54	-186.8626753	-186.824131
HCN	27	-93.45625859	-93.441723
CN	26	-92.73347225	-92.729601
H	1	-0.50215593	-0.502156

Table S4. Absolute energies and zero-point corrected energies (ZPE) for the most stable cations and neutral conformers from hypoxanthine calculated using B3LYP/6-311+G(2d,p).

Cation	Mass (*m/z*)	Absolute energy (h)	Zero-Point corrected energy (h)
$C_5H_4N_4O^+$	136	-487.0287338	-486.92981
$C_4H_2N_3O^+$	108	-392.8174957	-392.756789
$C_4H_4N_4^+$	108	-373.6346216	-373.546866
$C_3H_3N_3^+$	81	-280.0703798	-280.0703798
$C_3HN_2O^+$	81	-299.3307092	-299.29332
$C_3H_2N_3^+$	80	-279.4518876	-279.402985
$C_2H_2N_2^+$	54	-186.5514422	-186.515235
C_2NO^+	54	-205.8031015	-205.78799
$C_2HN_2^+$	53	-185.9467569	-185.921894
$HCNH^+$	28	-93.73493916	-93.709041
CO^+	28	-112.8300751	-112.824847
Neutral fragment	Mass (*m/z*)	Absolute energy (h)	Zero-Point corrected energy (h)
$C_4H_2N_3O$	108	-393.0282591	-392.971073
$C_4H_4N_4$	108	-373.9245758	-373.836136
$C_3H_3N_2O$	83	-300.9147819	-300.852479
$C_3H_4N_3$	82	-281.0267752	-280.952194
$C_2H_3N_2$	55	-187.4848886	-187.4848886
$C_2H_2N_2$	54	-186.9278986	-186.888652
HCNH	28	-94.00287677	-93.977139
CO	28	-113.3520125	-113.3520125
HCN	27	-93.441723	-93.441723
CN	26	-92.73347225	-92.729601
H	1	-0.50215593	-0.502156

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