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

Electronic Supplementary Information

QM/MM MD insight into photodynamics of hypoxanthine: distinct nonadiabatic decay behaviors between keto-N7H and keto-N9H tautomers in aqueous solution

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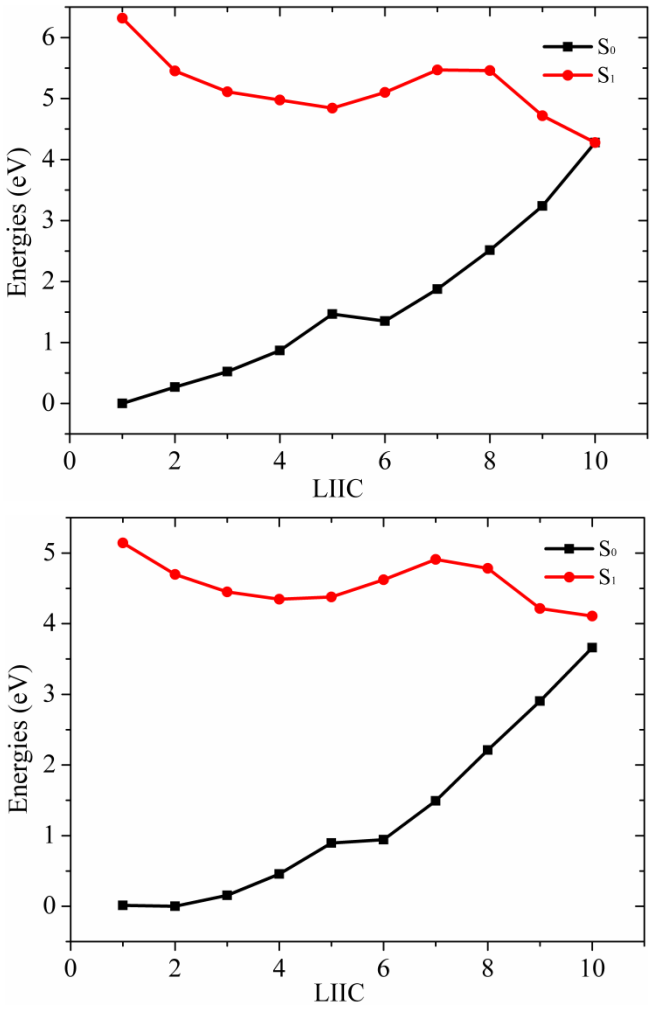

Fig. S1 Relative energy profiles along the LIIC reaction path from the S_0 state to conical intersection between S_0 and S_1 states of keto-N9H in the gas phase at both CASSCF (top) and CASPT2 (bottom) levels of theory, respectively.

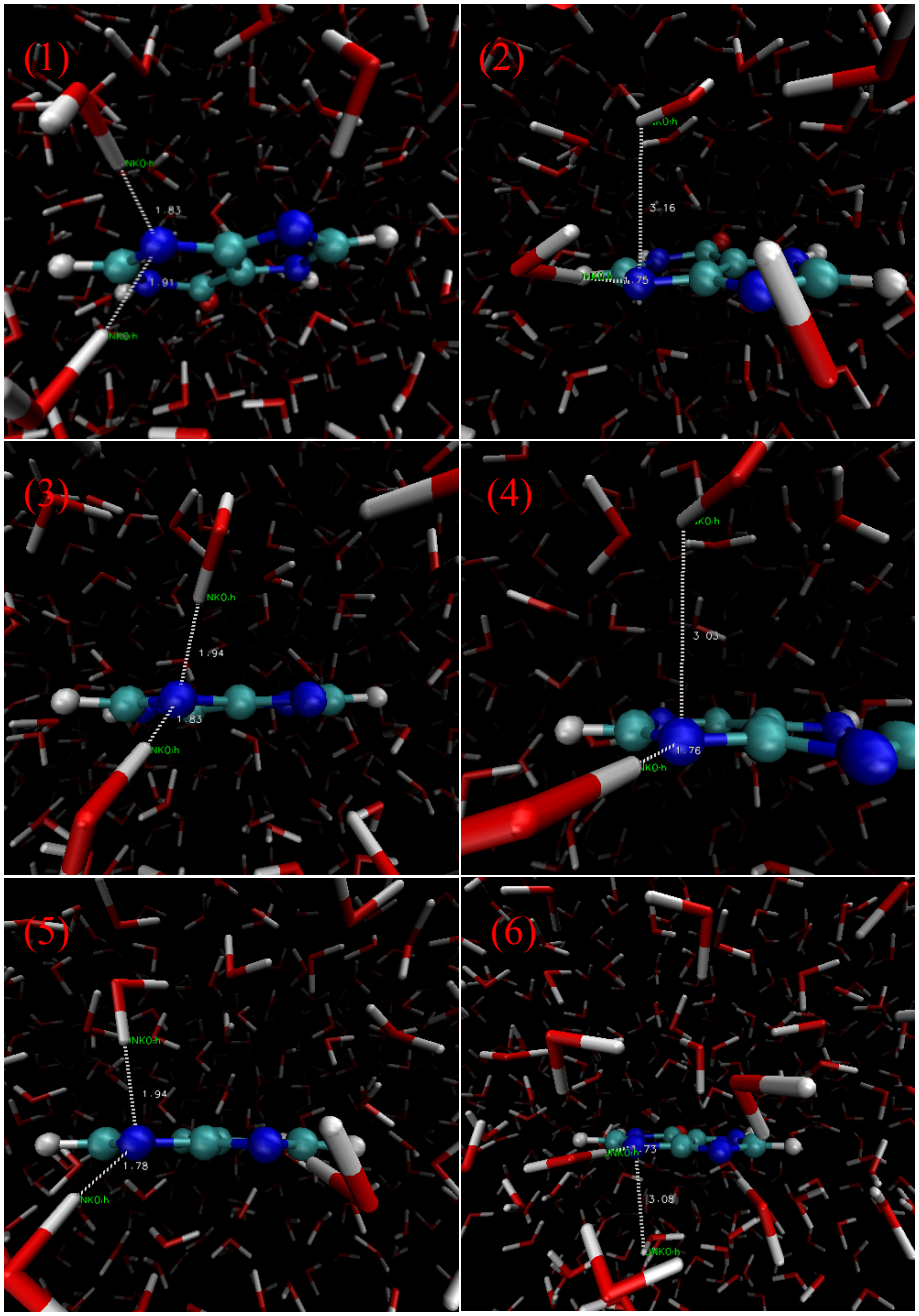

Fig. S2 QM/MM optimized 6 snapshot geometries of hypoxanthine keto-N7H tautomer in aqueous solution. At the N_3 site, each structure exhibits two intermolecular H-bonds including a π-electron H-bond.

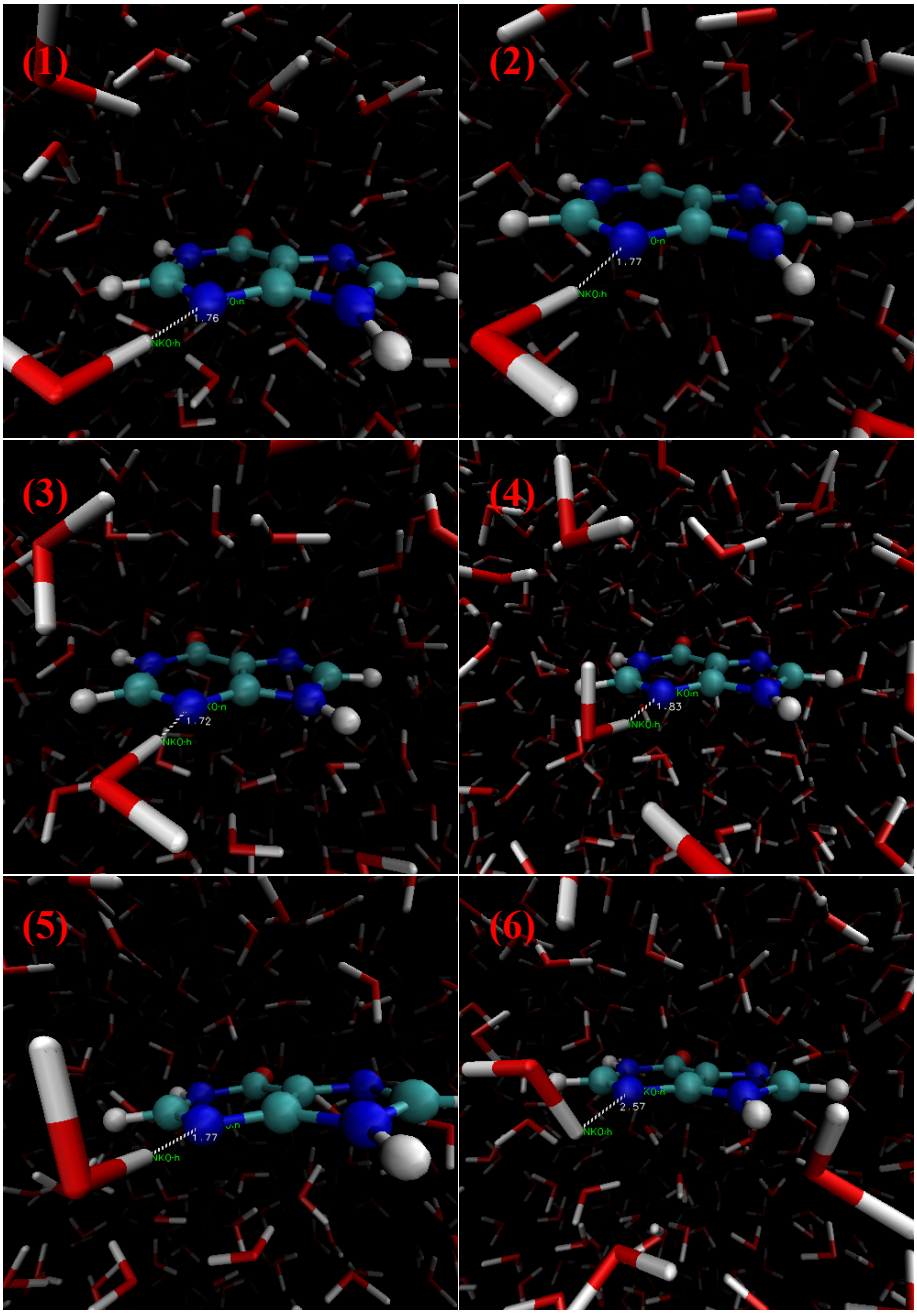

Fig. S3 QM/MM optimized 6 snapshot geometries of hypoxanthine keto-N9H tautomer in aqueous solution. At the N_3 site, each structure exhibits one intermolecular H-bond.

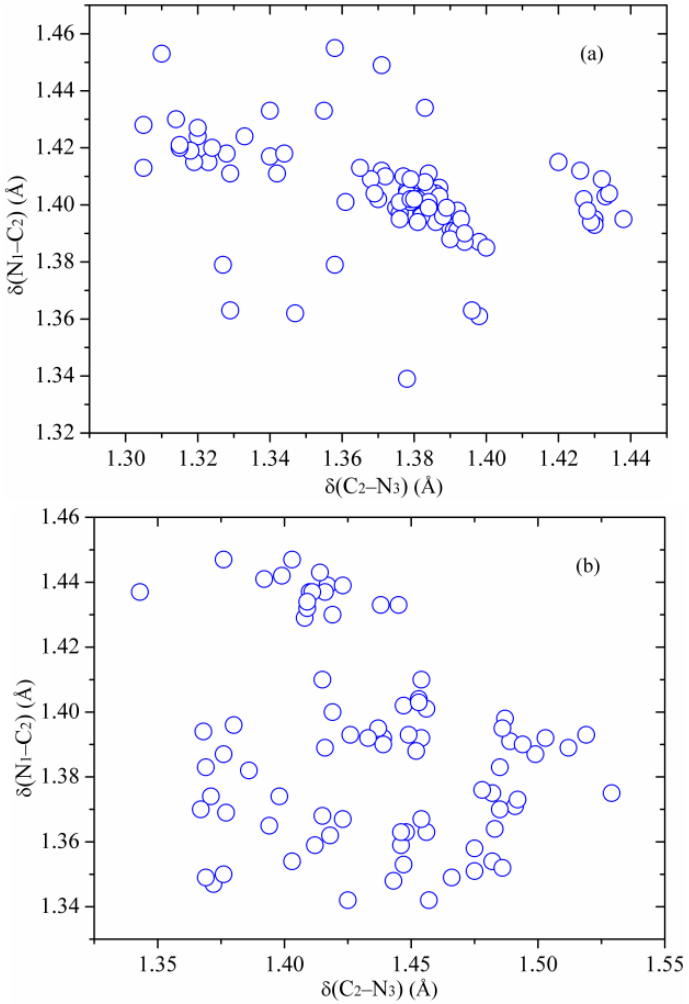

Fig. S4 Distributions of the $\delta(C_2–N_3)$ and $\delta(N_1–C_2)$ bond lengths of keto-N7H (a) and keto-N9H (b) at the $S_1 \rightarrow S_0$ hopping points.

Table S1 Key bond lengths (in angstroms), bond angles and dihedral angles (in degrees) in the optimized structures of keto-N7H and keto-N9H tautomers

	Vacuum[a]		Water[b]		Expt.[c]
	keto-N7H	keto-N9H	keto-N7H	keto-N9H	
N_1–C_2	1.377	1.365	1.362/1.355	1.358	1.367(2)
N_1–C_6	1.417	1.437	1.405/1.408	1.404	1.387(9)
C_2–N_3	1.293	1.300	1.306/1.307	1.307	1.298(7)
N_3–C_4	1.369	1.358	1.370/1.373	1.354	1.355(4)
C_4–C_5	1.401	1.400	1.399/1.400	1.400	1.385(3)
C_4–N_9	1.369	1.371	1.365/1.366	1.366	1.361(4)
C_5–C_6	1.439	1.452	1.431/1.435	1.440	1.410(10)
C_5–N_7	1.373	1.373	1.369/1.369	1.373	1.376(1)
C_6–O_6	1.219	1.211	1.227/1.223	1.231	1.247(1)
N_7–C_8	1.368	1.308	1.354/1.355	1.314	1.316(5)
C_8–N_9	1.315	1.380	1.324/1.327	1.369	1.362(14)
N_1–C_2–N_3	125.2	124.5	124.8/124.7	124.6	125.2(4)
N_1–C_6–C_5	108.1	108.7	109.2/108.8	110.0	111.7(2)
N_1–C_6–O_6	122.4	120.2	121.9/121.0	121.4	120.7(4)
C_2–N_1–C_6	125.5	126.6	125.5/126.2	126.0	124.5(5)
C_2–N_3–C_4	114.4	112.6	114.3/114.1	113.0	112.1(1)
N_3–C_4–C_5	123.5	128.5	123.6/123.7	126.9	127.5(3)
N_3–C_4–N_9	126.3	126.6	126.3/126.2	127.8	127.0(1)
C_4–C_5–C_6	123.3	119.1	122.5/122.4	119.5	119.2(3)
C_4–C_5–N_7	105.5	110.7	105.6/105.6	110.2	110.5(3)
C_4–N_9–C_8	104.9	106.6	104.7/104.7	106.8	106.8(2)
C_5–N_7–C_8	106.1	104.9	106.4/106.6	105.0	104.3(6)
C_5–C_6–O_6	129.5	131.1	128.9/130.1	128.7	127.7(3)
C_6–C_5–N_7	131.2	130.2	131.9/132.0	130.3	130.4(2)
N_7–C_8–N_9	113.3	112.9	113.2/113.1	112.7	112.9(4)
C_5–N_7–C_8–N_9	0.0	0.0	0.2/–0.7	0.2	-
C_6–C_5–C_4–N_9	180.0	180.0	178.0/178.3	177.9	-
H···N_3–C_4–C_5	-	-	111.4/–111.6	-	-
H···N_3–C_4–C_5	-	-	–165.8/151.3	–163.9	-

[a] B3LYP/def-SVP; [b] QM(B3LYP/def-SVP)/MM(TIP3P); [c] Experimental crystal data from ref. 11.

Table S2 Cartesian coordinates (Å) of the QMMM-optimized one representative ground-state geometry of keto-N7H. Only eight key water molecules are shown

Atom	X	Y	Z
C	0.048000	0.666000	1.630000
C	1.628000	0.572000	0.130000
C	1.762000	−0.462000	1.063000
C	3.610000	−1.230000	0.040000
C	2.561000	0.770000	−0.937000
N	0.763000	−0.389000	1.990000
N	0.525000	1.281000	0.522000
N	2.781000	−1.377000	1.038000
N	3.519000	−0.258000	−0.910000
O	2.593000	1.665000	−1.775000
H	−0.845000	1.025000	2.130000
H	0.185000	2.151000	0.099000
H	4.458000	−1.912000	−0.062000
H	4.207000	−0.220000	−1.672000
O	2.489000	−3.669000	2.649000
H	2.887000	−3.342000	3.477000
H	2.568000	−2.871000	2.081000
O	0.255000	3.837000	−0.654000
H	1.206000	4.013000	−0.423000
H	−0.153000	4.625000	−0.242000
O	4.761000	−1.271000	3.132000
H	4.035000	−1.238000	2.475000
H	4.382000	−1.915000	3.773000

O	4.790000	3.229000	−1.017000
H	5.632000	3.144000	−1.524000
H	4.237000	2.582000	−1.494000
O	4.944000	0.160000	−3.392000
H	5.727000	−0.182000	−2.905000
H	5.408000	0.693000	−4.085000
O	−0.101000	−2.278000	3.796000
H	0.311000	−1.538000	3.270000
H	−0.507000	−2.766000	3.033000
O	3.353000	3.293000	−3.832000
H	3.081000	2.551000	−3.248000
H	2.485000	3.746000	−3.942000
O	3.750000	−2.865000	5.040000
H	3.167000	−2.477000	5.749000
H	4.586000	−2.920000	5.578000

Table S3 Cartesian coordinates (Å) of the QMMM-optimized another representative ground-state geometry of keto-N7H. Only seven key water molecules are shown

Atom	X	Y	Z
C	0.237000	1.079000	0.956000
C	2.283000	1.594000	0.394000
C	2.231000	0.325000	0.984000
C	4.462000	0.084000	0.821000
C	3.515000	2.193000	−0.032000
N	0.991000	2.048000	0.384000
N	0.944000	0.019000	1.325000

N	3.334000	−0.469000	1.182000
N	4.575000	1.316000	0.269000
O	3.724000	3.279000	−0.555000
H	−0.835000	1.194000	1.103000
H	0.673000	2.956000	0.020000
H	5.403000	−0.460000	0.952000
H	5.511000	1.698000	0.082000
O	3.564000	−2.124000	3.371000
H	3.044000	−1.505000	3.947000
H	3.434000	−1.647000	2.508000
O	2.989000	−2.466000	−0.881000
H	2.440000	−1.877000	−1.457000
H	3.004000	−1.918000	−0.066000
O	−0.171000	−1.962000	2.889000
H	0.122000	−2.800000	2.450000
H	0.221000	−1.313000	2.247000
O	0.660000	4.792000	−0.300000
H	0.471000	5.207000	−1.175000
H	−0.080000	5.190000	0.221000
O	7.109000	2.504000	0.214000
H	7.547000	2.248000	1.060000
H	7.772000	2.161000	−0.426000
O	2.604000	4.120000	−2.863000
H	2.171000	3.231000	−2.887000
H	2.983000	4.075000	−1.953000

O	6.015000	−2.974000	2.045000
H	6.756000	−2.378000	2.315000
H	5.316000	−2.670000	2.655000
O	5.285000	−3.888000	−0.438000
H	5.516000	−3.574000	0.468000
H	4.448000	−3.385000	−0.575000

Table S4 Cartesian coordinates (Å) of the QMMM-optimized representative ground-state geometry of keto-N9H. Only seven key water molecules are shown

Atom	X	Y	Z
C	0.051000	−4.052000	−2.485000
C	−1.909000	−4.204000	−3.310000
C	−1.719000	−2.854000	−2.992000
C	−3.736000	−2.244000	−3.687000
C	−3.171000	−4.633000	−3.854000
N	−0.461000	−2.782000	−2.464000
N	−0.791000	−4.930000	−2.983000
N	−2.607000	−1.846000	−3.162000
N	−4.015000	−3.526000	−4.037000
O	−3.543000	−5.774000	−4.126000
H	−0.022000	−1.950000	−2.051000
H	1.059000	−4.269000	−2.132000
H	−4.544000	−1.529000	−3.852000

H	−4.947000	−3.688000	−4.443000
O	−2.445000	0.889000	−3.166000
H	−3.236000	0.989000	−3.739000
H	−2.389000	−0.104000	−3.163000
O	−6.304000	−2.888000	−5.562000
H	−7.094000	−2.316000	−5.437000
H	−6.706000	−3.602000	−6.118000
O	−3.683000	−7.839000	−5.863000
H	−3.729000	−7.024000	−5.307000
H	−2.945000	−7.608000	−6.450000
O	0.031000	−7.219000	−4.181000
H	−0.342000	−6.342000	−3.893000
H	0.990000	−7.001000	−4.054000
O	−5.206000	−7.151000	−2.316000
H	−4.697000	−7.769000	−1.745000
H	−4.468000	−6.680000	−2.759000
O	0.584000	−0.643000	−0.937000
H	0.852000	−0.819000	0.002000
H	1.394000	−0.152000	−1.227000
O	−1.698000	0.771000	−0.534000
H	−0.944000	0.152000	−0.686000
H	−2.050000	0.817000	−1.457000