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

Electronic Supplementary Information

UV-promoted radical formation, and near-IR-induced and spontaneous conformational isomerization in monomeric 9-methylguanine isolated in low-temperature Ar matrices

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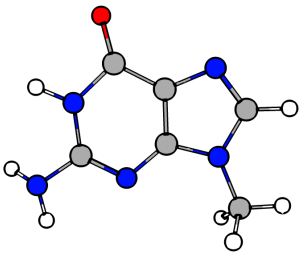
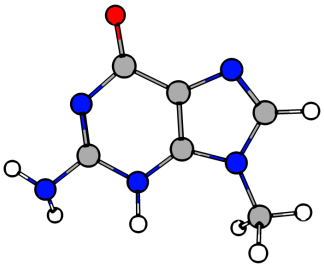
Table S1. Geometries of twenty-one isomers of 9-methylguanine (**9mG**) optimized at the DFT(B3LYP)/6-31++G(d,p) level of theory and their relative electronic energies (kJ mol^{-1}) calculated at the same level. Color codes: C – grey, H – white, N – blue, O – red.

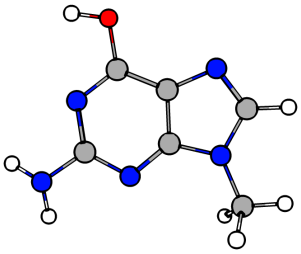
Main Canonical Forms



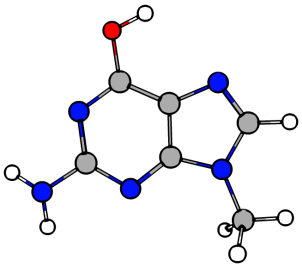
AO1 (AO)
0.00



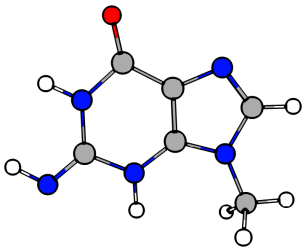
AO2
81.97



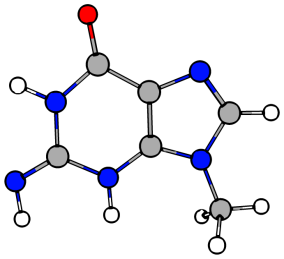
AH1
2.42



AH2
4.83



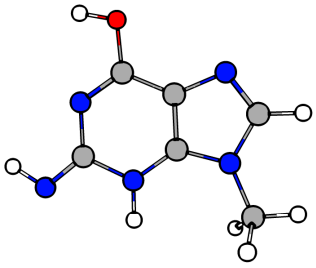
IO1
58.59



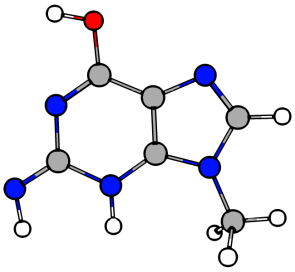
IO2
67.40

Table S1. Continued

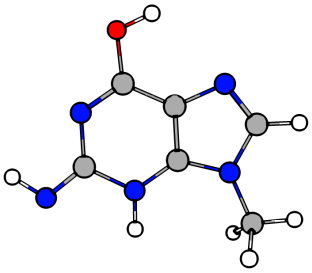
High-energy Canonical Forms



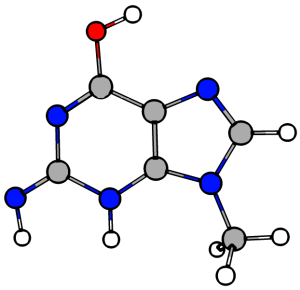
IH1
93.55



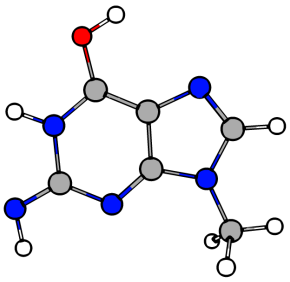
IH2
123.53



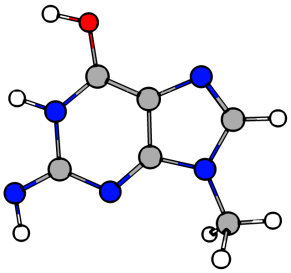
IH3
100.30



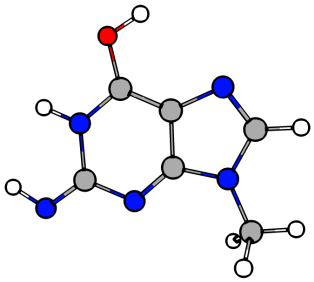
IH4
134.25



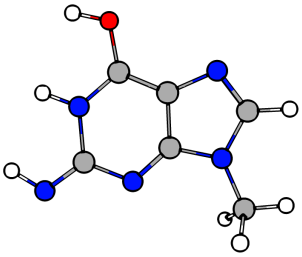
IH5
90.66



IH6
118.36



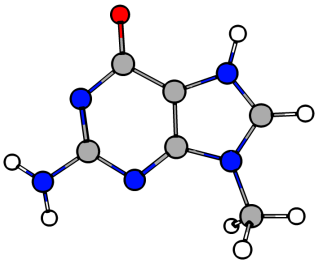
IH7
119.84



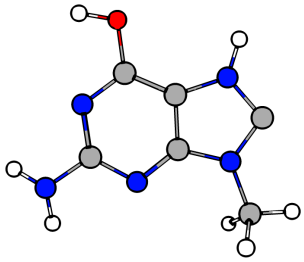
IH8
151.66

Table S1. Continued

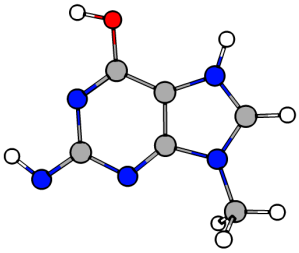
Non-Canonical Forms



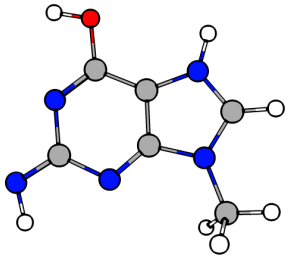
AO3
73.11



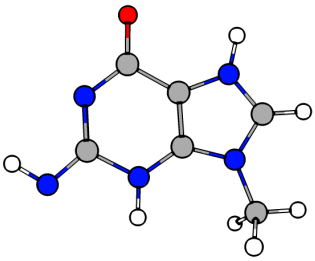
AH3
107.21



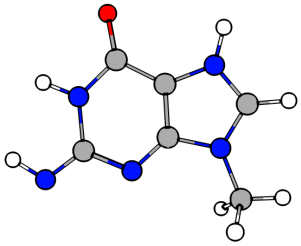
IH9
190.84



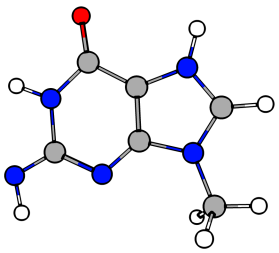
IH10
190.27



IO3
192.35



IO4
120.74



IO5
97.65

Table S2. comparison of the absorptions observed in the experimental mid-IR spectrum of **9mG** isolated in an Ar matrix at 14 K with the results of harmonic vibrational calculations carried out for the **AO**, **AH1** and **AH2** isomers of this molecule at the B3LYP/6-31++G(d,p) level of theory.

Experimental (Ar,14 K) [a]	Calculated [b]		Assignment [c]
	$\tilde{\nu}$	I	
3576	3585	87	νOH (**AH2**)
3571	3562	50	$\nu_a NH_2$ (**AH2**)
3568	3574	92	νOH (**AH1**)
3565	3557	44	$\nu_a NH_2$ (**AH1**)
3543/3535	3515	39	$\nu_a NH_2$ (**AO**)
3460/3454	3434	83	$\nu_s NH_2$ (**AH2**)
3458/3452	3431	72	$\nu_s NH_2$ (**AH1**)
3440/3435	3419	51	νN1H (**AO**)
3430/3427	3404	49	$\nu_s NH_2$ (**AO**)
1752/1741	1758	784	νC=O (**AO**)
1656			(**AH1**)
1652			(**AH2**)
1643/1640	1646	441	νC_5C_6; νC_4N_3 (**AH1**)
1640/1634	1645	494	νC_4N_3; νC_6N_1 (**AH2**)
1622	1633	473	νC_2N_3; δNH_2 (**AO**)
1608	1607	181	νC_2N_{10}; δNH_2 (**AH1**)
	1606	229	νC_2N_{10}; δNH_2 (**AH2**)
1598/1592	1590	494	νC_4N_3; νC_6N_1 (**AH2**)
1593/1589/1584	1592	430	νC_4N_3; νC_4C_5 (**AH1**)
1582	1587	218	νC_2N_3 (**AO**)
1575			(**AO**)
1561	1559	112	νC_4C_5; νC_4N_3 (**AO**)
1540	1539	111	νC_8N_7; νC_4N_9 (**AO**)
1524	1526	68	νC_8N_7; νC_4N_9 (**AH1**)
1522	1522	34	νC_8N_7; νC_4N_9 (**AH2**)
1492	1494	43	δCH_3 as; νC_6N_1 (**AH2**)
1483	1490	32	δCH_3 as; νC_6N_1 (**AH1**)
1472	1480	42	νC_6N_1; νC_4N_3 (**AH2**)
1467/1465	1472	161	νC_6N_1; νC_8N_7 (**AH1**)
1448/1445	1450	85	νC_6N_{10}; νC_8N_7 (**AH2**)
1441/1440	1446	79	νC_8N_7; νC_4N_9 (**AH1**)
1437/1435	1442	117	νC_2N_{10} (**AH1**)
1434/1431	1440	109	δCH_3 s (**AH2**)
1415/1412	1416	116	δCH_3 s (**AH1**)
1409/1408	1412	149	νC_4C_9; νC_8N_7 (**AH2**)
1376/1373	1369	42	νC_5C_6 (**AO**)
1336	1330	19	νC_8N_9; νC_5N_7 (**AO**)
1333	1331	48	νC_8N_9; νC_8N_7 (**AH2**)
1329	1328	34	νC_4C_5 (**AH1**)
1310	1306	51	δN_1H (**AO**)
1298	1294	86	νC_5N_7; νC_4N_3; νC_8N_9 (**AH2**)
1283/1275	1281	234	δOH (**AH2**)
1280/1277	1286	37	νC4N3; νC4N9; νC8N9 (**AH1**)

Table S2. Continued

Experimental (Ar,14 K) [a]	Calculated [b]		Assignment [c]
	$\tilde{\nu}$	I	
1239	1222	12	δC_8H (**AO**)
1225/1222	1221	42	δC_8H (**AH1**)
1205			(**AH1**)
1174	1195	184	δOH (**AH1**)
1137	1124	59	νC_2N_3; νC_5N_7; νC_6N_1 (**AO**)
1083/1080	1080	20	ρNH_2; νC_2N_3 (**AH1**)
1054	1048	10	νCO; νC_2N_3 (**AH1**)
1052	1046	36	νCO; νC_2N_3 (**AH2**)
1048	1039	41	ρCH_3 (**AO**)
1045/1044	1039	45	ρCH_3 (**AH2**)
1025			(**AO**)
1013	1007	17	δ ring (**AO**)
1005	994	76	δ ring (**AH1**)
1002	993	12	δ ring (**AH2**)
988			(**AH1**)
794	773	24	γ ring (**AH2**)
792	777	23	γ ring (**AH1**)
777	750	17	γ ring (**AO**)
726	719	10	δ ring (**AH2**)
725	718	16	δ ring (**AH1**)
722	716	24	δ ring (**AO**)
691/695	681	32	γ ring (**AO**)
673/668	667	18	$\delta N_{10}C_2N$; δOCN (**AH2**)
662	664	22	$\delta N_{10}C_2N$; δOCN (**AO**)
643/642	637	26	γ ring (**AO**)
634	631	34	γ ring (**AH1**)
631	626	15	γ ring (**AH2**)
586	583	72	γ N_1H (**AO**)
513/510	535	96	τOH (**AH1**)
507	517	111	τOH (**AH2**)

[a] Observed wavenumbers in cm^{-1}. [b] Calculated wavenumbers ($\tilde{\nu}$, cm^{-1}) are scaled by 0.95 and 0.98, above and below 3000 cm^{-1}, respectively, and calculated infrared intensities (I) are expressed in km mol^{-1}. [c] Assigning the experimental bands to a specific form was helped by the spectral changes resulting from the selective NIR irradiations and dark kinetics. Description of the vibrational modes was based on the vibrational analysis provided by the VibAnalysis software,[S1] supported by animation of the vibrations using the ChemCraft software.[S2] Abbreviations: ν, stretching; δ, in-plane deformation; γ, out-of-plane deformation ρ, rocking; τ, torsion; s, symmetric; a, antisymmetric. Experimental absorptions that do not have counterparts in harmonic vibrational calculations are assigned as (**AH1**), (**AH2**) or (**AO**), depending on their behaviour upon the NIR irradiations and dark kinetics. See Figure S1 for the atom numbering scheme.

Supporting References:

S1. G. A. Zhurko *Chemcraft - Graphical Program for Visualization of Quantum Chemistry Computations*, Version 1.8; http://www.chemcraftprog.com, 2015.

S2. (a) F. Teixeira, *VibAnalysis - Tools for performing vibrational analysis on molecular systems*, https://github.com/teixeirafilipe/vibAnalysis, 2019; (b) F. Teixeira and M. Cordeiro, *J. Chem. Theory Comput*., 2019, **15**, 456-470.

Table S3. Anharmonic wavenumbers ($\tilde{\nu}$, unscaled) and IR intensities (I) calculated for first overtones of the OH, NH and NH_2 stretching vibrations, and combination tones involving the symmetric and antisymmetric NH_2 stretching vibrations. Anharmonic vibrational calculations were carried out at the B3LYP/6-31++G(d,p) level of theory for the **AO**, **AH1** and **AH2** isomeric forms of **9mG**.

Isomer	Vibrational mode	$\tilde{\nu}$ / cm^{-1}	I / km mol^{-1}
AO	$2\nu_aNH_2$	6981.221	2.341
	$(\nu_a+\nu_s)$ NH_2	6826.379	2.099
	$2\nu_sNH_2$	6799.100	2.389
	2νN1H	6726.461	2.992
AH1	$2\nu_aNH_2$	7091.334	2.316
	2νOH	6964.016	6.389
	$(\nu_a+\nu_s)$ NH_2	6917.521	1.987
	$2\nu_sNH_2$	6870.379	1.981
AH2	$2\nu_aNH_2$	7106.455	2.340
	2νOH	7000.517	4.270
	$(\nu_a+\nu_s)$ NH_2	6928.913	2.012
	$2\nu_sNH_2$	6878.006	1.994

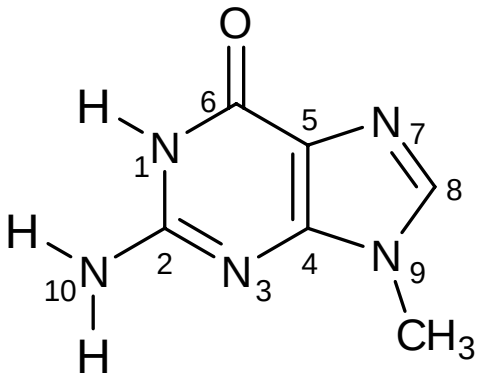


Figure S1. Molecular structure of 9-methylguanine (**9mG**) in the amino-oxo (**AO**) form, including the numbering of selected atoms.

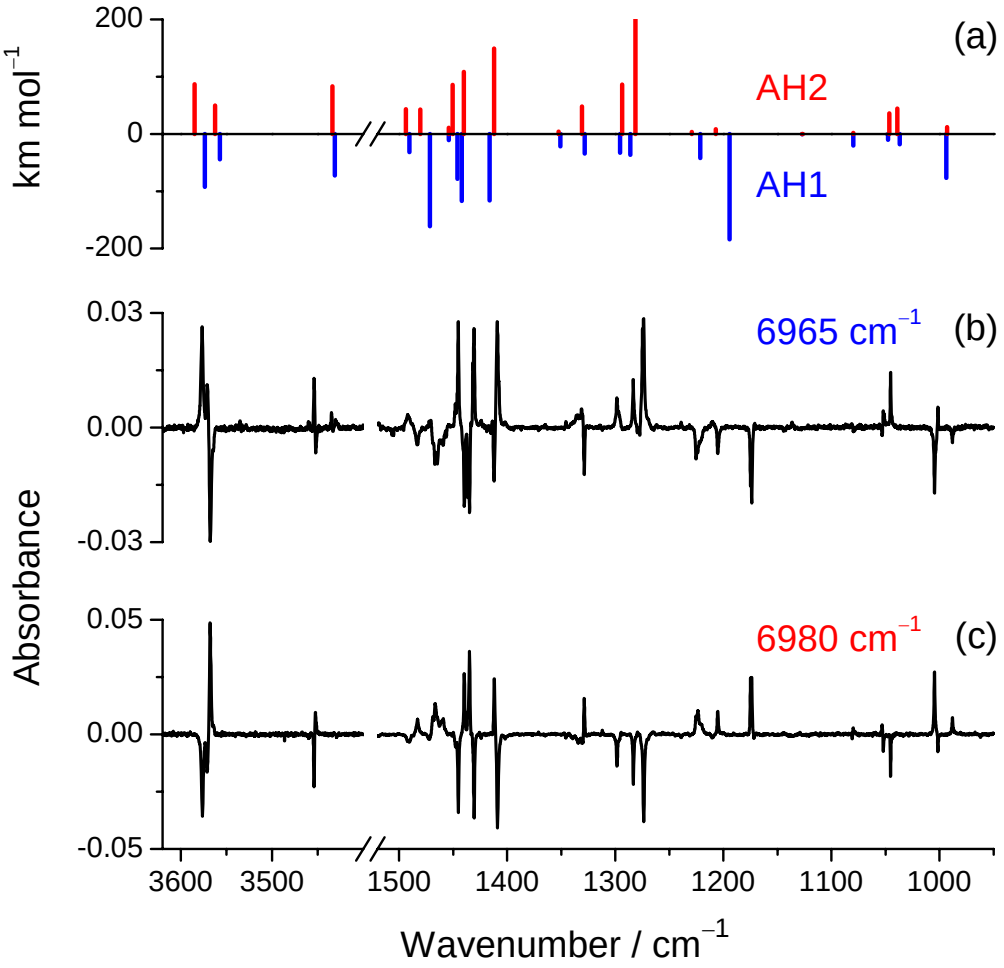


Figure S2. (a) Mid-IR spectra of (red) **AH2** and (blue) **AH1** conformers of the amino-hydroxy tautomer of 9-methylguanine (**9mG**) theoretically calculated at the DFT(B3LYP)/6-31++G(d,p) level. The IR intensities computed for **AH1** were multiplied by −1. The theoretical wavenumbers were scaled by 0.98; (b) experimental difference spectrum: the spectrum recorded after irradiation of matrix-isolated **9mG** at 6965 cm^{-1} *minus* the spectrum recorded before that irradiation; (c) experimental difference spectrum: the spectrum recorded after irradiation of matrix-isolated **9mG** at 6980 cm^{-1} *minus* the spectrum recorded before that irradiation.

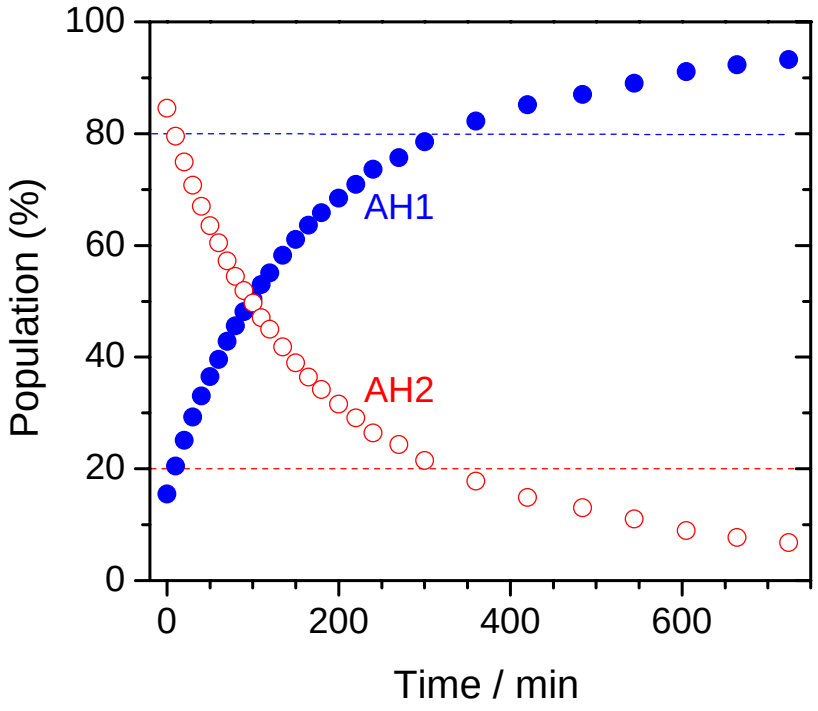


Figure S3. Time evolution of the populations of the **AH1** (closed blue circles) and **AH2** (open red circles) conformers of **9mG** trapped in an Ar matrix at 12 K by keeping the matrix in dark for 720 minutes. The initial conformational composition was obtained by irradiating the matrix at wavenumbers within the 6966-6956 cm^{-1} range for several minutes. The populations of the two forms were estimated from integration of the 1448/1445 (**AH2**) and 1441/1440 (**AH1**) pairs of doublets. Horizontal dashed lines represent the relative abundances estimated for the two conformers (**AH1** : **AH2** relates as 80 : 20) at the photostationary state (compare with Fig. 6 of the main text).

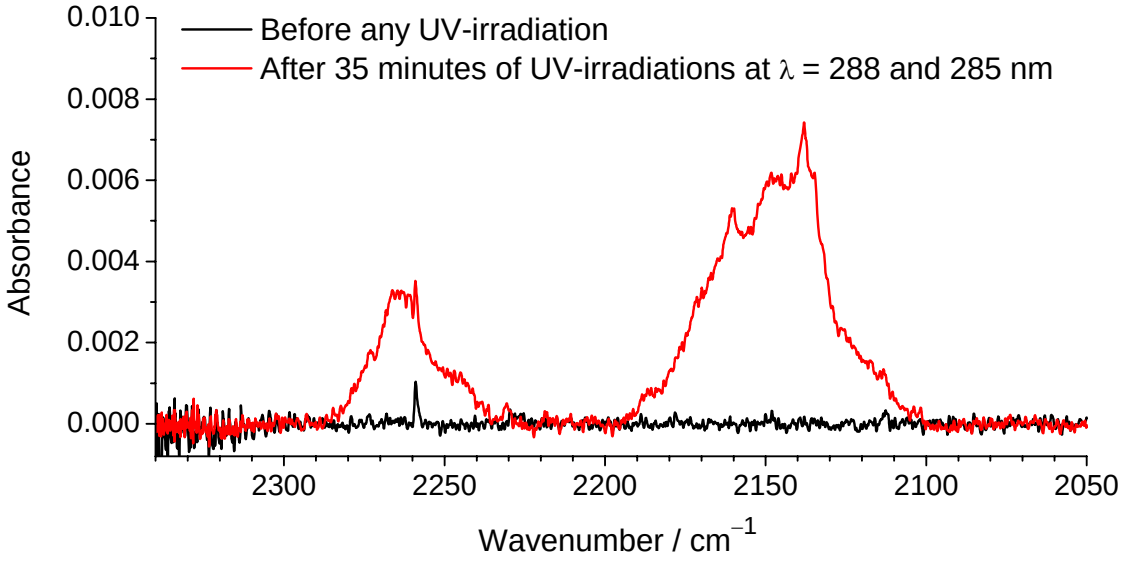


Figure S4. Fragment of the IR spectra of **9mG** isolated in an argon matrix: (black) the spectrum recorded before any UV-irradiation; (red) the spectrum recorded after 35 minutes of UV-irradiations at λ = 288 and 285 nm. The higher- and lower-frequency bands are spectral indications of formation of open-ring isocyanates and ketenes, respectively. The lower-frequency band may also include the contribution of carbon monoxide generated in photodecomposition processes.