Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Mode-specific vibrational relaxation of photoexcited guanosine 5'-monophosphate and its acid form: A femtosecond broadband mid-IR transient absorption and theoretical study

Electronic Supplementary Information

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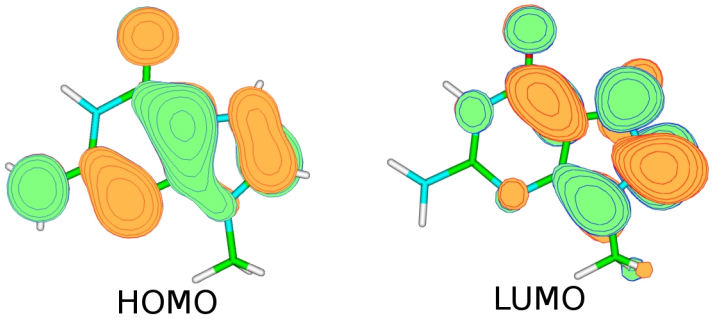

Fig. S1 Depiction of the frontier orbitals of $GN7D^+$, involved in the $L_a \leftarrow S_0$ excitation. Protonation does not alter qualitatively the shape of the orbitals (compare with Fig. S8 in reference 20 of the main text).

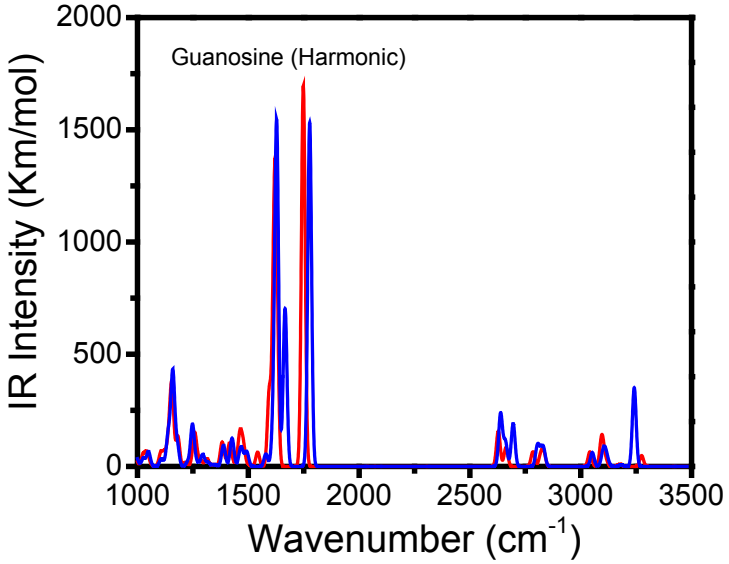

Fig. S2 IR spectra computed in D_2O by PCM/PBE0/6-31+G(d) calculations in the region 1000-3500 cm^{-1} for the ground state minimum of ribose-G (red curves) and ribose-GN7D$^+$ (blue curves). Intensity computed at the harmonic level.

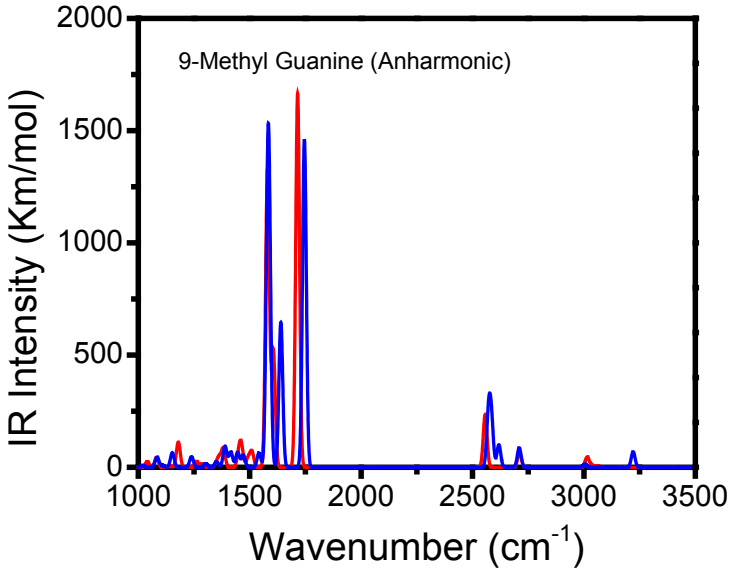

Fig. S3 IR spectra computed in D_2O by PCM/PBE0/6-31+G(d) calculations in the region 1000-3500 cm^{-1} for the ground state minimum of 9Me-G (red curves) and 9Me-GN7D$^+$ (blue curves). Intensity computed at the anharmonic level.

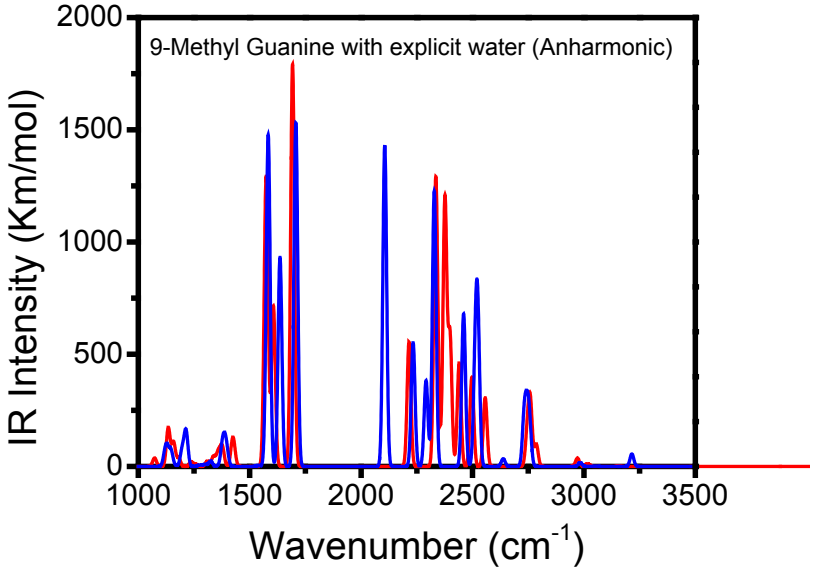

Fig. S4 IR spectra computed in D_2O by PCM/PBE0/6-31+G(d) calculations in the region 1000-3500 cm^{-1} for the ground state minimum of 9Me-G·5D_2O (red curves) and 9Me-GN7D$^+$·5D_2O (blue curves). Intensity computed at the anharmonic level.

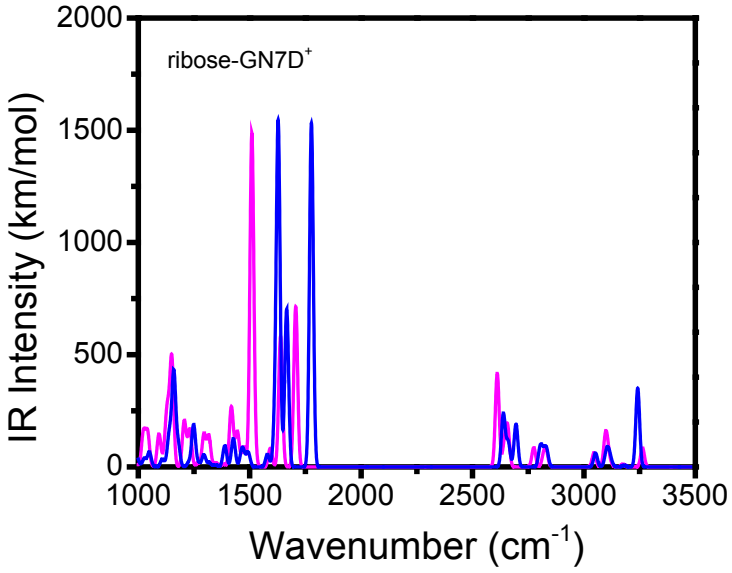

Fig. S5 Harmonic PCM/PBE0/6-31+G(d) calculated IR spectra in D_2O for the ground (blue) and $S_1(L_a)$ excited state (magenta) for ribose-GN7D$^+$. Each stick transition was broadened using a Gaussian with FWHM=10 cm^{-1}.

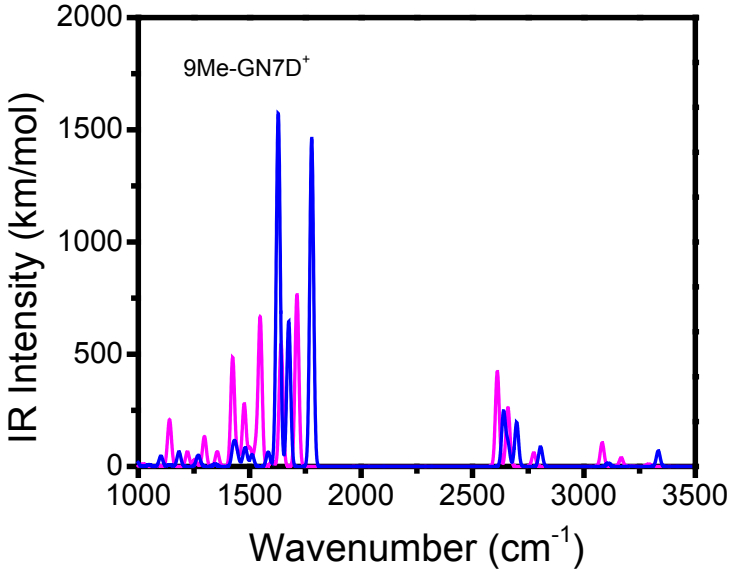

Fig. S6 Harmonic PCM/PBE0/6-31+G(d) calculated IR spectra in D_2O for the ground (blue) and $S_1(L_a)$ excited state (magenta) for 9Me-GN7D$^+$. Each stick transition was broadened using a Gaussian with FWHM=10 cm^{-1}.

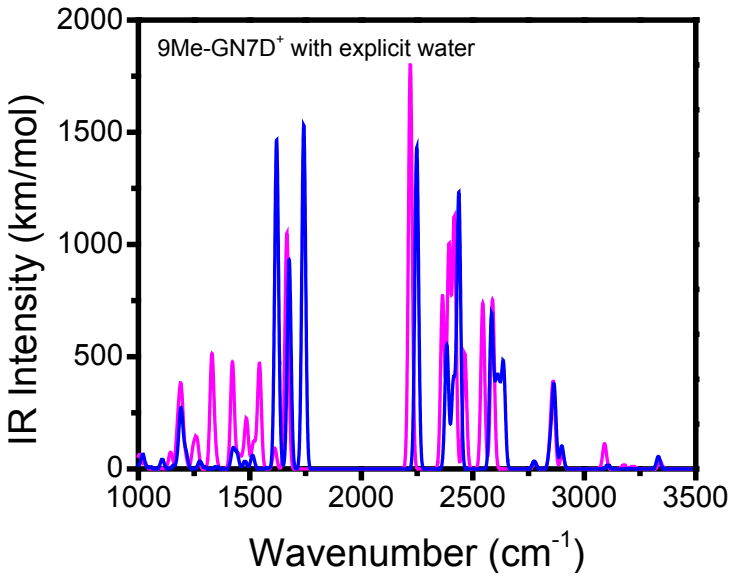

Fig. S7 Harmonic PCM/PBE0/6-31+G(d) calculated IR spectra in D_2O for the ground (blue) and $S_1(L_a)$ excited state (magenta) for 9Me-GN7D$^+$·5D_2O. Each stick transition was broadened using a Gaussian with FWHM=10 cm^{-1}.

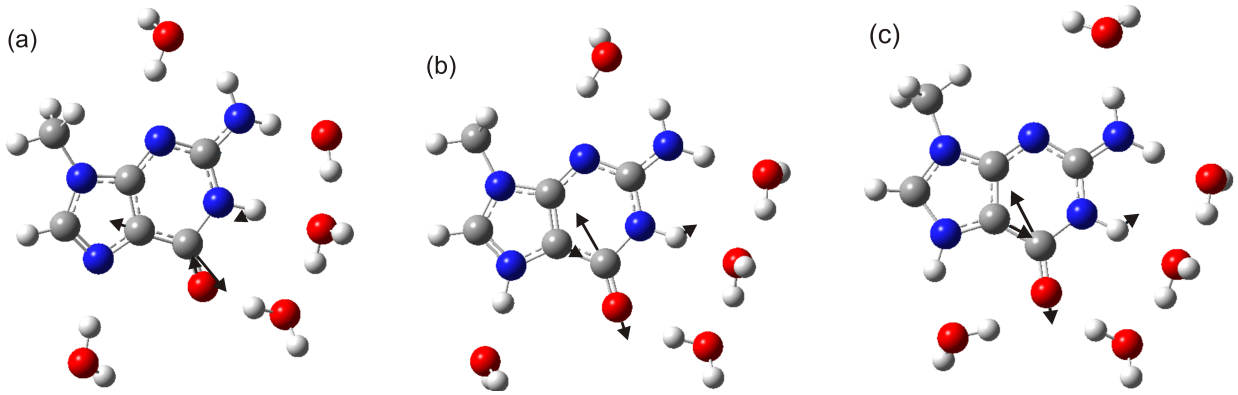

Figure S8. C=O stretching modes for (a) ground state 9Me-G·5D_2O, (b) ground state 9Me-GN7D^+·5D_2O, and (c) 9Me-GN7D^+·5D_2O L_a state.

Cartesian Coordinates of the L_a excited state minimum computed for the species ribose-GN7D$^+$ by LR-PCM/TD-PBE0/6-31+G(d,p) calculations. SCF energy= -963.026304590 a.u.

6	-0.008325	-0.019012	-0.002862
6	-0.009931	0.028993	1.417265
6	1.203636	0.035716	2.121788
7	2.411866	0.009715	1.584272
6	2.428477	-0.022166	0.226071
7	1.309857	-0.023790	-0.525689
7	-1.043536	-0.017257	2.333697
6	-0.446956	0.140259	3.606911
7	0.920564	0.083402	3.457906
6	1.884643	0.066036	4.541469
6	1.716863	1.225933	5.523036
6	2.132157	0.605349	6.849528
6	1.686387	-0.850024	6.697477
8	1.707532	-1.121758	5.287236
6	0.329493	-1.174414	7.285674
8	-0.641195	-0.269281	6.782252
8	3.542641	0.590201	7.020218
7	3.624578	-0.045131	-0.335115
8	-0.980683	-0.044060	-0.757474
1	-1.490325	-0.469678	7.190387
1	0.402681	-1.103965	8.379564
1	0.072850	-2.209056	7.023208
1	2.866845	0.064022	4.059836
1	2.323285	2.091445	5.246473
1	0.666779	1.527813	5.567822
1	1.643926	1.090394	7.702549
1	3.851536	1.499954	7.102538
1	-0.934031	-0.090910	4.546160
1	2.424549	-1.505065	7.173904
1	3.766506	-0.064421	-1.335550
1	4.435691	-0.041502	0.268863
1	1.371016	-0.042898	-1.537928
1	-1.939723	0.410595	2.131683

Cartesian Coordinates of the L_a excited state minimum computed for the species GN7D$^+$ by LR-PCM/TD-PBE0/6-31+G(d,p) eq calculations. SCF energy= -581.713074040 a.u.

7	0.001263	-0.002780	-0.001477
6	-0.009610	-0.013022	1.359815
6	1.322009	0.006013	1.813421
7	2.145418	-0.040419	0.709781
6	1.303635	0.089309	-0.419945
7	-1.087904	-0.023253	2.127118
6	-0.833733	-0.028355	3.461111
7	0.411219	-0.021643	3.978543
6	1.602224	-0.021067	3.205578
8	2.704618	-0.027264	3.756711
7	-1.895725	-0.034694	4.247958
6	-1.158448	0.039614	-0.867558
1	-1.839712	-0.034339	5.256950
1	-2.809495	-0.038599	3.814839
1	0.550310	-0.023609	4.983126
1	1.617887	-0.152325	-1.425437
1	-1.079220	-0.747388	-1.620625
1	-2.047542	-0.122814	-0.260104
1	-1.219939	1.014510	-1.359499
1	3.071398	0.369068	0.717566

Cartesian Coordinates of the L_a excited state minimum computed for the species $GN7D^+$ by LR-PCM/TD-PBE0/6-31+G(d,p) neq calculations. SCF energy= -581.712000093 a.u.

7	0.000490	-0.015483	-0.000622
6	-0.005526	-0.015181	1.360672
6	1.320640	0.005594	1.813188
7	2.154607	-0.059576	0.707637
6	1.305387	0.074397	-0.416223
7	-1.087457	-0.026786	2.128998
6	-0.833075	-0.027526	3.461904
7	0.412066	-0.020159	3.979491
6	1.602034	-0.024741	3.205025
8	2.701959	-0.034612	3.755528
7	-1.896406	-0.031537	4.248313
6	-1.157604	0.039738	-0.867483
1	-1.841462	-0.028340	5.257520
1	-2.809806	-0.036712	3.813966
1	0.552420	-0.020570	4.983971
1	1.617213	-0.145857	-1.426776
1	-1.079768	-0.740164	-1.628043
1	-2.048440	-0.126344	-0.263480
1	-1.216148	1.019447	-1.350627
1	3.057530	0.401356	0.714914

Cartesian Coordinates of the L_a excited state minimum computed for the species $GN7D^+ \cdot 5D_2O$ by LR-PCM/TD-PBE0/6-31+G(d,p) neq calculations. SCF energy= -963.567503839 a.u.

7	2.487593	1.839551	-0.001574
6	1.289680	1.204973	-0.054810
6	1.530816	-0.180272	-0.100678
7	2.889829	-0.349542	-0.107270
6	3.481041	0.905914	0.017740
7	0.084783	1.775923	-0.012230
6	-0.945324	0.899914	-0.049968
7	-0.802380	-0.449630	-0.125931
6	0.449399	-1.092854	-0.128140
8	0.526410	-2.351292	-0.152014
7	-2.155631	1.428852	0.005882
6	2.687766	3.274730	0.068812
8	-4.437191	-0.089545	0.236427
8	-2.999297	-2.230238	-0.554414
8	-1.483562	-4.021916	0.664290
8	3.188418	-3.107149	0.011399
8	-2.376175	4.210274	0.099842
1	-3.022387	0.853248	0.078487
1	-2.223781	2.461637	0.053173
1	-1.629464	-1.049498	-0.283130
1	4.526636	1.119241	-0.130396
1	1.711361	3.756591	0.076209
1	3.258175	3.608788	-0.800490
1	3.230131	3.522334	0.983866
1	2.209936	-3.058128	-0.010821
1	3.417011	-3.580434	0.818117
1	-0.678864	-3.524631	0.398341
1	-1.379415	-4.917232	0.325160
1	-3.143695	-2.465854	-1.477752
1	-2.595458	-3.024032	-0.117232
1	-4.124416	-1.001506	0.063055
1	-4.853842	-0.098828	1.104716
1	-1.597009	4.663940	0.441252
1	-3.122234	4.571819	0.591732
1	3.344393	-1.264528	-0.003498

Complete citation for reference 43 of the main text:

Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.