

*Electronic Supplemental Information for...*

## “Mechanisms and Energetics for N-Glycosidic Bond Cleavage of Protonated 2'-Deoxyguanosine and Guanosine”

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**Data Handling.** Ion intensities, measured as a function of collision energy, are converted to absolute cross sections. Limitations in the pressure measurement, and uncertainties in the length of interaction region, lead to uncertainties in the CID cross section magnitudes. The uncertainty in relative cross sections is approximately  $\pm 5\%$  and that for the absolute cross sections is approximately  $\pm 20\%$ . The ion kinetic energy distribution is measured to be Gaussian and has a typical fwhm of 0.2 – 0.5 eV (lab). Uncertainties in the absolute energy scale are approximately  $\pm 0.05$  eV (lab). Zero-pressure extrapolated CID cross sections correct for the effects of multiple collisions, which can significantly influence the shape of CID cross sections even when the pressure of Xe is kept low as multiple energizing collisions can shift the “apparent threshold” to lower energies.

**Thermochemical Analysis.** In eq 1,  $\sigma_0$  is an energy independent scaling factor,  $E$  is the relative translational energy of the reactants,  $E_0$  is the threshold for reaction of the ground electronic and ro-vibrational state, and  $n$  is an adjustable parameter that describes the efficiency of kinetic to internal energy transfer.<sup>1</sup> The summation is over the ro-vibrational states of the reactant ions,  $[\text{dGuo}+\text{H}]^+$  and  $[\text{Guo}+\text{H}]^+$ , where  $E_i$  is the excitation energy of each state, and  $g_i$  is the population of those states ( $\sum g_i = 1$ ). Because the protonated nucleosides of interest in this study possess many low-frequency vibrational modes, the populations of excited vibrational modes are not insignificant even at 298 K. Thus, the internal energy of the protonated nucleoside contributes appreciably to the dissociation threshold. The relative reactivity of all ro-vibrational states of the protonated nucleoside, as reflected by the fitting parameters,  $\sigma_0$  and  $n$ , is assumed to be equivalent. Whether the dissociation of the protonated nucleoside occurs within the time scale of the experiments,  $\sim 10^{-4}$  s, must be taken into account in the thermochemical analysis of the CID data. If the lifetime of the activated  $[\text{dGuo}+\text{H}]^+$  or  $[\text{Guo}+\text{H}]^+$  complex exceeds this time frame, the apparent thresholds shift to higher energies, resulting in a kinetic shift. Therefore, the CID data was analyzed by including Rice-Ramsperger-Kassel-Marcus (RRKM) theory into eq 1 as described in detail elsewhere.<sup>2,3</sup> The statistical model of eq 1 is modified to eq 2 to incorporate competitions observed for various dissociation pathways.<sup>4</sup> The parameters of eq 2 are generally the same as in eq 1,  $\tau$  is the experimental time available for dissociation, and  $k$  is the unimolecular dissociation rate constant.  $\Delta E$  is the energy that remains in translation after the collision between the reactants. The term  $(E + E_i - \Delta E)$  is the internal energy of the energized protonated nucleoside after the collision with Xe. The indices  $j$  refer to the individual dissociation channels and  $k_j$  is the unimolecular rate constant for channel  $j$ . To ensure appropriate treatment of the effects of competition, analyses must include all important dissociation pathways such that  $(\sum k_j = k_{\text{tot}})$ . The scaling factors,  $\sigma_{0,j}$ , are ideally the same for all product channels.

However, independent scaling was required to reproduce the data with high fidelity. Eq 2 reduces to the modified form of eq 1 that includes lifetime effects when there is only one dissociation pathway. Inclusion of lifetime and competitive effects in eqs 1 and 2 requires sets of ro-vibrational frequencies for the protonated nucleoside and the rate-limiting transition states (TSs) leading to N-glycosidic bond cleavage. For the activated N-glycosidic bond cleavage processes investigated here, the tight TSs associated with these pathways are explicitly modeled theoretically to determine appropriate molecular parameters for the thermochemical analysis of the experimental data. Before comparison to the experimental data, eqs 1 and 2 are convoluted with the kinetic energy distributions of the reactants, and a nonlinear least-squares analysis of the data is performed to determine optimized values for the parameters,  $\sigma_0$ ,  $E_0$  and  $n$ .

In this study, N-glycosidic bond cleavage produces the protonated nucleobase,  $[\text{Gua}+\text{H}]^+$ , from  $[\text{dGuo}+\text{H}]^+$  and  $[\text{Guo}+\text{H}]^+$ . According to the theoretically predicted PESs, two tight TSs,  $\text{TS}_1$  associated with glycosidic bond elongation and  $\text{TS}_2$  associated with transfer of the 2'-proton from the sugar to the nucleobase guanine, must be overcome, which exceed the final reaction enthalpy (including BSSE corrections). In particular, for production of  $[\text{Gua}+\text{H}]^+$  from  $[\text{dGuo}+\text{H}]^+$ , B3LYP finds  $\text{TS}_1$  as the rate-determining step, whereas MP2 suggests that  $\text{TS}_2$  is the rate-limiting step. The molecular parameters of both  $\text{TS}_1$  and  $\text{TS}_2$  leading to the elimination of  $[\text{Gua}+\text{H}]^+$  from  $[\text{dGuo}+\text{H}]^+$  and  $[\text{Guo}+\text{H}]^+$  are therefore examined to accurately determine which TS provides the best reproduction and interpretation of the CID data. Because elimination of  $[\text{Gua}+\text{H}]^+$  is the lowest and most favorable dissociation pathway, the total CID cross sections are also modeled using the parameters for this dissociation pathway. For the elimination of the neutral nucleobase Gua, producing  $[\text{dGuo-Gua}+\text{H}]^+$  and  $[\text{Guo-Gua}+\text{H}]^+$ , theory suggests that these dissociation processes occurs by TSs also involving glycosidic bond elongation,  $\text{TS}_n$ , that differ from  $\text{TS}_1$ , and lie more than 50 kJ/mol lower in energy than the product dissociation asymptote (including BSSE corrections). The relatively large energy difference between  $\text{TS}_n$  and the dissociation asymptote suggests that a PSL TS may be most appropriate. However, the tight TS,  $\text{TS}_n$  and a switching TS (incorporating molecular parameters of both  $\text{TS}_n$  and the PSL TS) models are also used to analyze the threshold regions for this dissociation channel to ensure that the most appropriate TS model is accurately determined.

The Beyer-Swinehart algorithm is used to evaluate the density of ro-vibrational states,<sup>5-7</sup> and the relative populations,  $g_i$ , are calculated for a Maxwell-Boltzmann distribution at 298 K, the internal temperature of the reactant ions. The average internal energies at 298 K of the reactant ions,  $[\text{dGuo}+\text{H}]^+$  and  $[\text{Guo}+\text{H}]^+$ , TSs and CID products are also given in Table S1. The errors in the measured thresholds are estimated from the range of values determined for the zero-pressure-extrapolated data sets, variations associated with uncertainties in the vibrational frequencies (prescaled by 0.99) and estimated by  $\pm 10\%$  scaling of all frequencies, and the error in the absolute energy scale,  $\pm 0.02$  eV (CM). For analyses that include the RRKM lifetime analysis, the uncertainties in the measured thresholds also include the effects of increasing and decreasing the time assumed available for dissociation by a factor of 2.

**References**

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**Table S1.** Vibrational Frequencies and Average Internal Energies of the Ground-State Conformations of the Reactants, and Transition States (including PSL TS CID Products) for N-Glycosidic Bond Cleavage of [dGuo+H]<sup>+</sup> and [Guo+H]<sup>+</sup>.

Species	E <sub>vib</sub> , eV <sup>a</sup>	Vibrational frequencies, cm <sup>-1b</sup>
[dGuo+H] <sup>+</sup>	0.44 (0.04)	28, 47, 85, 97, 122, 141, 142, 169, 185, 199, 225, 239, 260, 271, 297, 300, 326, 354, 373, 430, 453, 465, 485, 559, 572, 592, 619, 638, 646, 658, 670, 681, 703, 728, 759, 770, 831, 849, 867, 917, 947, 954, 1005, 1010, 1038, 1045, 1061, 1067, 1096, 1107, 1121, 1130, 1146, 1177, 1197, 1233, 1238, 1268, 1274, 1280, 1306, 1330, 1340, 1347, 1353, 1384, 1394, 1426, 1434, 1440, 1474, 1479, 1487, 1534, 1558, 1594, 1620, 1656, 1788, 2999, 3008, 3024, 3039, 3044, 3071, 3094, 3155, 3534, 3567, 3573, 3688, 3804, 3806
[dGuo+H] <sup>+</sup> _TS <sub>1</sub>	0.45 (0.04)	20, 22, 43, 63, 92, 117, 140, 146, 153, 187, 197, 235, 249, 306, 311, 319, 337, 364, 381, 392, 428, 436, 487, 532, 552, 594, 618, 622, 644, 668, 678, 705, 724, 741, 760, 776, 821, 838, 861, 868, 928, 958, 959, 965, 1007, 1028, 1052, 1068, 1085, 1109, 1112, 1125, 1176, 1183, 1200, 1226, 1247, 1263, 1267, 1284, 1316, 1331, 1340, 1357, 1367, 1386, 1394, 1422, 1438, 1452, 1476, 1491, 1533, 1554, 1574, 1607, 1649, 1779, 2844, 2975, 3014, 3038, 3063, 3101, 3207, 3222, 3544, 3562, 3593, 3669, 3794, 3807
[dGuo+H] <sup>+</sup> _TS <sub>2</sub>	0.46 (0.04)	11, 25, 35, 50, 73, 99, 139, 144, 158, 182, 193, 223, 239, 243, 293, 306, 339, 355, 361, 378, 433, 453, 486, 543, 565, 605, 619, 628, 642, 649, 668, 705, 727, 737, 763, 783, 808, 837, 856, 860, 896, 960, 966, 992, 1005, 1020, 1050, 1069, 1076, 1085, 1102, 1112, 1131, 1183, 1191, 1216, 1239, 1253, 1264, 1274, 1291, 1319, 1338, 1349, 1360, 1372, 1403, 1422, 1428, 1442, 1464, 1487, 1489, 1550, 1573, 1588, 1603, 1651, 1776, 2988, 3036, 3040, 3086, 3093, 3160, 3242, 3542, 3568, 3585, 3685, 3794, 3804
[dGuo+H] <sup>+</sup> _TS <sub>n</sub>	0.46 (0.04)	15, 26, 40, 54, 85, 103, 137, 145, 153, 182, 188, 238, 266, 300, 305, 311, 338, 365, 366, 378, 422, 429, 487, 534, 551, 596, 622, 624, 645, 668, 684, 706, 708, 726, 764, 779, 831, 834, 854, 870, 927, 957, 960, 971, 1002, 1024, 1048, 1071, 1085, 1103, 1113, 1127, 1175, 1178, 1193, 1223, 1247, 1262, 1263, 1286, 1313, 1330, 1334, 1353, 1359, 1381, 1386, 1419, 1435, 1456, 1476, 1490, 1535, 1572, 1576, 1605, 1647, 1775, 2884, 2980, 3028, 3047, 3057, 3110, 3159, 3218, 3544, 3564, 3593, 3674, 3792, 3809
[Guo+H] <sup>+</sup>	0.47 (0.04)	26, 47, 71, 90, 114, 134, 141, 155, 181, 190, 221, 229, 250, 277, 280, 289, 305, 311, 336, 357, 381, 429, 462, 481, 491, 556, 561, 591, 619, 628, 653, 660, 662, 700, 702, 728, 756, 765, 794, 846, 859, 875, 909, 942, 986, 1007, 1014, 1046, 1054, 1067, 1089, 1097, 1118, 1128, 1133, 1145, 1186, 1198, 1233, 1241, 1260, 1273, 1292, 1307, 1324, 1333, 1353, 1357, 1368, 1381, 1393, 1420, 1431, 1435, 1475, 1488, 1534, 1558, 1594, 1621, 1656, 1787, 2994, 2998, 3029, 3041, 3043, 3078, 3163, 3534, 3565, 3573, 3687, 3707, 3803, 3807
[Guo+H] <sup>+</sup> _TS <sub>1</sub>	0.49 (0.04)	16, 25, 39, 56, 72, 87, 122, 142, 147, 153, 180, 189, 213, 265, 290, 305, 313, 338, 345, 358, 367, 442, 448, 488, 494, 533, 546, 555, 593, 619, 624, 644, 668, 678, 707, 719, 726, 762, 763, 833, 845, 859, 885, 931, 958, 967, 1019, 1027, 1041, 1069, 1085, 1102, 1108, 1125, 1135, 1175, 1180, 1192, 1226, 1248, 1254, 1267, 1288, 1309, 1328, 1334, 1352, 1356, 1387, 1405, 1414, 1433, 1452, 1475, 1490, 1532, 1571, 1574, 1606, 1648, 1776, 2898, 2974, 3021, 3087, 3111, 3171, 3221, 3545, 3561, 3595, 3667, 3706, 3810, 3811
[Guo+H] <sup>+</sup> _TS <sub>2</sub>	0.49 (0.04)	19, 25, 32, 67, 73, 96, 128, 143, 162, 180, 189, 203, 245, 262, 275, 280, 289, 328, 346, 362, 372, 408, 430, 442, 459, 487, 544, 553, 562, 601, 627, 645, 652, 665, 703, 714, 727, 732, 765, 776, 836, 849, 878, 912, 970, 987, 996, 1021, 1044, 1064, 1071, 1105, 1118, 1129, 1159, 1178, 1187, 1198, 1213, 1244, 1257, 1259, 1279, 1307, 1336, 1342, 1351, 1359, 1390, 1398, 1409, 1432, 1440, 1464, 1489, 1491, 1549, 1584, 1598, 1617, 1650, 1778, 2972, 3022, 3064, 3089, 3176, 3234, 3541, 3568, 3586, 3681, 3721, 3806, 3809

**Table S1.** (cont'd.) Vibrational Frequencies and Average Internal Energies of the Ground-State Conformations of the Reactants, and Transition States (including PSL TS CID Products) for N-Glycosidic Bond Cleavage of [dGuo+H]<sup>+</sup> and [Guo+H]<sup>+</sup>.

Species	E <sub>vib</sub> , eV <sup>a</sup>	Vibrational frequencies, cm <sup>-1b</sup>
[Guo+H] <sup>+</sup> _TS <sub>n</sub>	0.47 (0.04)	21, 29, 73, 83, 106, 112, 143, 144, 162, 189, 214, 224, 226, 262, 286, 307, 335, 347, 355, 365, 389, 397, 465, 490, 535, 559, 564, 604, 619, 624, 647, 669, 703, 706, 720, 733, 759, 778, 779, 840, 855, 874, 885, 931, 959, 964, 1023, 1028, 1041, 1072, 1099, 1115, 1117, 1122, 1159, 1179, 1193, 1210, 1242, 1258, 1262, 1283, 1299, 1316, 1332, 1342, 1350, 1369, 1385, 1402, 1440, 1462, 1478, 1483, 1489, 1533, 1551, 1583, 1607, 1655, 1782, 2981, 3018, 3021, 3033, 3105, 3216, 3225, 3319, 3542, 3571, 3587, 3685, 3751, 3804
Gua	0.19 (0.02)	141, 148, 189, 302, 320, 332, 364, 484, 488, 533, 579, 580, 624, 636, 668, 713, 727, 763, 826, 851, 949, 1023, 1077, 1094, 1138, 1174, 1269, 1311, 1359, 1385, 1440, 1464, 1533, 1553, 1607, 1648, 1749, 3210, 3532, 3556, 3611, 3636
[dGuo-Gua+H] <sup>+</sup>	0.19 (0.02)	98, 140, 173, 214, 283, 320, 358, 376, 412, 615, 656, 737, 777, 833, 865, 928, 948, 968, 989, 1053, 1095, 1105, 1185, 1195, 1222, 1236, 1249, 1285, 1303, 1332, 1352, 1378, 1420, 1433, 1489, 1600, 2986, 2990, 3033, 3057, 3065, 3119, 3135, 3791, 3798
[Guo-Gua+H] <sup>+</sup>	0.22 (0.02)	88, 107, 160, 187, 221, 288, 316, 345, 353, 435, 488, 558, 607, 679, 735, 766, 840, 898, 944, 973, 1029, 1050, 1084, 1100, 1136, 1179, 1198, 1221, 1243, 1253, 1287, 1297, 1329, 1337, 1377, 1412, 1432, 1490, 1603, 2984, 3001, 3031, 3081, 3118, 3132, 3689, 3794, 3799

<sup>a</sup>Present results, uncertainties are listed in parentheses. <sup>b</sup>Vibrational frequencies scaled by 0.99 obtained from vibrational analysis of the geometry optimized structures determined at the B3LYP/6-311+G(d,p) level of theory.

**Table S2.** Rotational Constants of [dGuo+H]<sup>+</sup> and [Guo+H]<sup>+</sup> and the Transition States for N-Glycosidic Bond Cleavage Reactions.

Reactant	Ionic Product	Energized Molecule		Transition State			
		1-D <sup>a</sup>	2-D <sup>b</sup>	1-D <sup>c</sup>	2-D <sup>c</sup>	2-D <sup>d</sup>	
[dGuo+H] <sup>+</sup>	[Gua+H] <sup>+</sup>	0.026	0.067	TS <sub>1</sub>	0.023	0.0069	-
				TS <sub>2</sub>	0.024	0.0057	-
	[dGuo-Gua+H] <sup>+</sup>	0.026	0.067	TS <sub>n</sub>	0.022	0.0060	-
				PSL	0.10, 0.064	0.058, 0.030	0.0012
[Guo+H] <sup>+</sup>	[Gua+H] <sup>+</sup>	0.022	0.063	TS <sub>1</sub>	0.020	0.0059	-
				TS <sub>2</sub>	0.020	0.062	-
	[Guo-Gua+H] <sup>+</sup>	0.022	0.063	TS <sub>n</sub>	0.021	0.0061	-
				PSL	0.085, 0.064	0.043, 0.030	0.0012

<sup>a</sup>Active external. <sup>b</sup>Inactive external. <sup>c</sup>Rotational constants of the TS treated as free internal rotors. <sup>d</sup>Two-dimensional rotational constant of the TS at threshold, treated variantionally and statistically.

**Table S3.** Fragments Observed Arising from Sequential Dissociation of [dGuo-Gua+H]<sup>+</sup> and [Guo-Gua+H]<sup>+</sup>.

	m/z	Chemical Formula	Symbol <sup>a</sup>	Neutral Loss <sup>b</sup>
[dGuo-Gua+H] <sup>+</sup>	99	C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> <sup>+</sup>	▽	H <sub>2</sub> O
m/z = 117	81	C <sub>5</sub> H <sub>5</sub> O <sup>+</sup>	◇	2H <sub>2</sub> O
C <sub>5</sub> H <sub>9</sub> O <sub>3</sub> <sup>+</sup>	67	C <sub>4</sub> H <sub>3</sub> O <sup>+</sup>	△	H <sub>2</sub> O, CH <sub>4</sub> O
	55	C <sub>3</sub> H <sub>3</sub> O <sup>+</sup>	○	2H <sub>2</sub> O, C <sub>2</sub> H <sub>2</sub>
	41	C <sub>2</sub> HO <sup>+</sup>	□	H <sub>2</sub> O, CH <sub>4</sub> O, C <sub>2</sub> H <sub>2</sub>
[Guo-Gua+H] <sup>+</sup>	115	C <sub>5</sub> H <sub>7</sub> O <sub>3</sub> <sup>+</sup>	▽	H <sub>2</sub> O
m/z = 133	97	C <sub>5</sub> H <sub>5</sub> O <sub>2</sub> <sup>+</sup>	◇	2H <sub>2</sub> O
C <sub>5</sub> H <sub>9</sub> O <sub>4</sub> <sup>+</sup>	83	C <sub>4</sub> H <sub>3</sub> O <sub>2</sub> <sup>+</sup>	△	H <sub>2</sub> O, CH <sub>4</sub> O
	71	C <sub>3</sub> H <sub>3</sub> O <sub>2</sub> <sup>+</sup>	○	2H <sub>2</sub> O, C <sub>2</sub> H <sub>2</sub>
	53	C <sub>3</sub> HO <sup>+</sup>	□	H <sub>2</sub> O, CH <sub>4</sub> O, CH <sub>2</sub> O
	41	C <sub>2</sub> HO <sup>+</sup>	★	2H <sub>2</sub> O, C <sub>2</sub> H <sub>2</sub> , CH <sub>2</sub> O

<sup>a</sup>Listed symbols correspond to those displayed in Figure 2. <sup>b</sup>Proposed sequential neutral losses from the primary [dGuo-Gua+H]<sup>+</sup> and [Guo-Gua+H]<sup>+</sup> CID products.

**Table S4.** Fitting Parameters of Equation 1, Activation Energies and Reaction Enthalpies at 0 K, and Entropies of Activation at 1000 K of [dGuo+H]<sup>+</sup> Obtained from Independent Threshold Analyses for N-Glycosidic Bond Cleavage of [dGuo+H]<sup>+</sup><sup>a</sup>

Cross Section	TS	Energy Range	$\sigma_0$	$n$	$E_0$ (eV)	$\Delta S_{1000}^\ddagger$ (J mol <sup>-1</sup> K <sup>-1</sup> )
Total	TS <sub>1</sub>	0.45(0.08)–2.83(0.06)	87.4 (6.6)	2.1 (0.1)	0.99 (0.03)	25 (1)
	TS <sub>2</sub>	0.45(0.08)–2.80(0.03)	80.2 (4.6)	2.2 (0.1)	1.02 (0.03)	46 (1)
	no RRKM	0.45(0.08)–2.80(0.03)	69.4 (3.7)	2.2 (0.1)	1.49 (0.05)	-
[Gua+H] <sup>+</sup>	TS <sub>1</sub>	0.43(0.05)–2.71(0.03)	81.0 (7.5)	2.1 (0.1)	0.98 (0.03)	25 (1)
	TS <sub>2</sub>	0.43(0.05)–2.71(0.03)	77.0 (6.6)	2.2 (0.1)	1.02 (0.03)	46 (1)
	no RRKM	0.43(0.05)–2.71(0.03)	66.4 (6.1)	2.3 (0.1)	1.47 (0.05)	-
[dGuo-Gua+H] <sup>+</sup>	TS <sub>n</sub>	0.82(0.17)–4.46(0.14)	84.8 (4.0)	1.0 (0.1)	1.65 (0.05)	32 (1)
	PSL	0.82(0.17)–4.42(0.15)	73.1 (4.9)	1.2 (0.1)	2.17 (0.06)	98 (4)
	SW	0.87(0.07)–4.44(0.14)	73.4 (3.5)	1.2 (0.1)	2.17 (0.07)	98 (4)
	no RRKM	0.87(0.07)–4.44(0.14)	64.7 (3.8)	1.3 (0.1)	3.08 (0.06)	-

<sup>a</sup>Average values, uncertainties are listed in parentheses.

**Table S5.** Fitting Parameters of Equation 1, Activation Energies and Reaction Enthalpies at 0 K, and Entropies of Activation at 1000 K of  $[\text{Guo}+\text{H}]^+$  Obtained from Independent Threshold Analyses for N-Glycosidic Bond Cleavage of  $[\text{Guo}+\text{H}]^{+a}$ 

Cross Section	TS	Energy Range	$\sigma_0$	$n$	$E_0$ (eV)	$\Delta S_{1000}^+$ ( $\text{J mol}^{-1} \text{K}^{-1}$ )
Total	TS <sub>1</sub>	0.69(0.10)–3.81(0.05)	79.7 (5.4)	2.1 (0.1)	1.21 (0.04)	36 (1)
	TS <sub>2</sub>	0.69(0.10)–3.81(0.05)	79.3 (5.8)	2.1 (0.1)	1.20 (0.04)	38 (1)
	no RRKM	0.69(0.10)–3.81(0.05)	65.0 (4.3)	2.2 (0.1)	2.03 (0.06)	-
$[\text{Gua}+\text{H}]^+$	TS <sub>1</sub>	0.48(0.08)–3.53(0.03)	61.7 (3.6)	2.3 (0.1)	1.17 (0.03)	36 (1)
	TS <sub>2</sub>	0.48(0.08)–3.53(0.03)	62.2 (3.6)	2.3 (0.1)	1.16 (0.03)	38 (1)
	no RRKM	0.48(0.08)–3.53(0.03)	49.7 (0.1)	2.4 (0.1)	1.94 (0.05)	-
$[\text{Guo-Gua}+\text{H}]^+$	TS <sub>n</sub>	0.91 (0.10)–5.45 (0.11)	36.5 (4.0)	1.1 (0.1)	1.69 (0.06)	3 (1)
	PSL	0.85(0.08)–5.50(0.19)	28.1 (3.7)	1.3 (0.1)	2.45 (0.08)	100 (4)
	SW	0.82(0.06)–5.57(0.09)	28.1 (1.6)	1.2 (0.1)	2.45 (0.08)	100 (4)
	no RRKM		23.9 (1.5)	1.4 (0.1)	3.79 (0.06)	-

<sup>a</sup>Average values, uncertainties are listed in parentheses.**Table S6.** Fitting Parameters of Equation 2, Activation Energies and Reaction Enthalpies at 0 K, and Entropies of Activation at 1000 K of  $[\text{dGuo}+\text{H}]^+$  Obtained from Competitive Threshold Analyses for N-Glycosidic Bond Cleavage of  $[\text{dGuo}+\text{H}]^{+a}$ 

Cross Section	TS	Energy Range	$\sigma_0$	$n$	$E_0$ (eV)	$\Delta S_{1000}^+$ ( $\text{J mol}^{-1} \text{K}^{-1}$ )
$[\text{Gua}+\text{H}]^+$	TS <sub>1</sub>	0.69(0.10)–2.85(0.06)	83.1 (5.8)	2.1 (0.1)	0.98 (0.02)	25 (1)
$[\text{dGuo-Gua}+\text{H}]^+$	PSL		1.3 (0.1)		1.73 (0.04)	99 (4)
$[\text{Gua}+\text{H}]^+$	TS <sub>2</sub>	0.59(0.15)–2.80(0.02)	73.5 (5.7)	2.2 (0.1)	1.01 (0.03)	46 (1)
$[\text{dGuo-Gua}+\text{H}]^+$	PSL		2.4 (1.0)		1.69 (0.04)	99 (4)
$[\text{Gua}+\text{H}]^+$	TS <sub>1</sub>	0.54(0.07)–2.72(0.02)	83.3 (4.2)	2.1 (0.1)	0.98 (0.03)	25 (1)
$[\text{dGuo-Gua}+\text{H}]^+$	TS <sub>n</sub>		1.6 (0.8) e <sup>4</sup>		1.60 (0.03)	32 (1)
$[\text{Gua}+\text{H}]^+$	TS <sub>2</sub>	0.54(0.07)–2.70(0.02)	76.8 (3.5)	2.2 (0.1)	1.02 (0.03)	46 (1)
$[\text{dGuo-Gua}+\text{H}]^+$	TS <sub>n</sub>		1.2 (0.6) e <sup>5</sup>		1.63 (0.03)	32 (1)
$[\text{Gua}+\text{H}]^+$	TS <sub>1</sub>	0.64(0.10)–2.91(0.04)	79.1 (4.2)	2.1 (0.1)	0.97 (0.03)	25 (1)
$[\text{dGuo-Gua}+\text{H}]^+$	SW		1.3 (0.2)		1.72 (0.04)	99 (4)
$[\text{Gua}+\text{H}]^+$	TS <sub>2</sub>	0.66(0.10)–2.88(0.05)	71.3 (6.6)	2.2 (0.1)	1.00 (0.02)	46 (1)
$[\text{dGuo-Gua}+\text{H}]^+$	SW		2.7 (0.7)		1.69 (0.04)	99 (4)

<sup>a</sup>Average values, uncertainties are listed in parentheses.

**Table S7.** Fitting Parameters of Equation 2, Activation Energies and Reaction Enthalpies at 0 K, and Entropies of Activation at 1000 K of  $[\text{Guo}+\text{H}]^+$  Obtained from Competitive Threshold Analyses for N-Glycosidic Bond Cleavage of  $[\text{Guo}+\text{H}]^{+a}$ 

Cross Section	TS	Energy Range	$\sigma_0$	$n$	$E_0$ (eV)	$\Delta S_{1000}^+$ ( $\text{J mol}^{-1} \text{K}^{-1}$ )
$[\text{Gua}+\text{H}]^+$	$\text{TS}_1$	0.72(0.05)–3.78(0.04)	75.2 (3.1)	2.1 (0.1)	1.20 (0.04)	36 (1)
$[\text{Guo-Gua}+\text{H}]^+$	PSL		0.9 (0.4)		2.02 (0.05)	101 (4)
$[\text{Gua}+\text{H}]^+$	$\text{TS}_2$	0.78(0.06)–3.86(0.06)	75.2 (3.9)	2.1 (0.1)	1.19 (0.04)	38 (1)
$[\text{Guo-Gua}+\text{H}]^+$	PSL		0.9 (0.1)		2.01 (0.06)	101 (4)
$[\text{Gua}+\text{H}]^+$	$\text{TS}_1$	0.77(0.06)–3.72(0.03)	77.7 (2.3)	2.1 (0.1)	1.21 (0.03)	36 (1)
$[\text{Guo-Gua}+\text{H}]^+$	$\text{TS}_n$		$4.8 (4.1) e^5$		1.91 (0.07)	3 (1)
$[\text{Gua}+\text{H}]^+$	$\text{TS}_2$	0.79(0.05)–3.72(0.03)	77.4 (2.7)	2.1 (0.1)	1.20 (0.03)	38 (1)
$[\text{Guo-Gua}+\text{H}]^+$	$\text{TS}_n$		$6.2 (6.1) e^5$		1.92 (0.07)	3 (1)
$[\text{Gua}+\text{H}]^+$	$\text{TS}_1$	0.79(0.10)–3.82(0.04)	72.7 (1.8)	2.1 (0.1)	1.20 (0.03)	36 (1)
$[\text{Guo-Gua}+\text{H}]^+$	SW		0.9 (0.1)		2.01 (0.06)	101 (4)
$[\text{Gua}+\text{H}]^+$	$\text{TS}_2$	0.79(0.10)–3.82(0.02)	73.4 (3.0)	2.1 (0.1)	1.19 (0.03)	38 (1)
$[\text{Guo-Gua}+\text{H}]^+$	SW		0.9 (0.1)		2.01 (0.06)	101 (4)

<sup>a</sup>Average values, uncertainties are listed in parentheses.**Table S8.** Fitting Parameters of Equation 2, Activation Energies and Reaction Enthalpies at 0 K, and Entropies of Activation at 1000 K of  $[\text{dGuo}/\text{Guo}+\text{H}]^+$  Obtained from Competitive Threshold Analyses for N-Glycosidic Bond Cleavage of  $[\text{dGuo}/\text{Guo}+\text{H}]^{+a}$ 

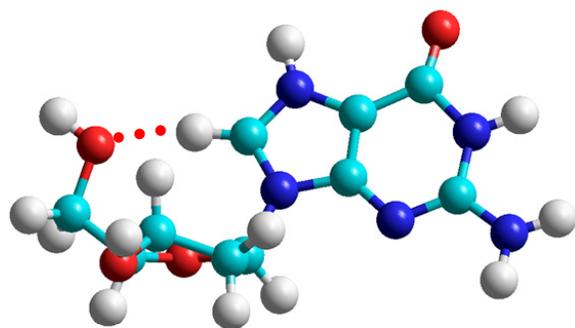
Cross Section	TS	Energy Range	$\sigma_0$	$n$	$E_0$ (eV)	$\Delta S_{1000}^+$ ( $\text{J mol}^{-1} \text{K}^{-1}$ )
$[\text{Gua}+\text{H}]^+$	$\text{TS}_1$	0.62(0.07)–2.91(0.04)	76.2 (6.7)	2.2 (0.1)	0.97 (0.02)	25 (1)
$[\text{dGuo-Gua}+\text{H}]^+$	$\text{SW}^b$		1.3 (0.3)		1.71 (0.04)	99 (4)
$[\text{Gua}+\text{H}]^+$	$\text{TS}_1$	0.68(0.08)–2.82(0.03)	72.8 (1.7)	2.1 (0.1)	1.20 (0.04)	36 (1)
$[\text{Guo-Gua}+\text{H}]^+$	$\text{SW}^b$		1.0 (0.2)		2.01 (0.06)	101 (4)

<sup>a</sup>Average values, uncertainties are listed in parentheses. <sup>b</sup>SW= $\text{TS}_1$  and PSL**Table S9.** Enthalpies and Free Energies of Activated Dissociation for Glycosidic Bond Cleavage of  $[\text{dGuo}+\text{H}]^+$  and  $[\text{Guo}+\text{H}]^+$  at 0 and 298 K in kJ/mol.<sup>a</sup>

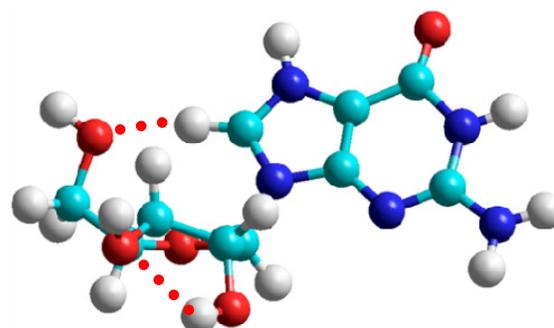
Reactant	CID Product	$\Delta H_0$	$\Delta H_0^b$	$\Delta H_{298}-\Delta H_0^b$	$\Delta H_{298}$	$\Delta H_{298}^b$	$T\Delta S_{298}^b$	$\Delta G_{298}$	$\Delta G_{298}^b$
$[\text{dGuo}+\text{H}]^+$	$[\text{Gua}+\text{H}]^+$	93.6 (2.9)	95.2	3.8 (2.6)	97.4 (3.9)	99.0	8.0 (4.0)	89.4 (5.6)	91.0
	$[\text{dGuo-Gua}+\text{H}]^+$	166.0 (3.9)	157.6	0.5 (3.6)	166.5 (5.3)	158.1	54.3 (8.5)	112.2 (10.0)	103.8
$[\text{Guo}+\text{H}]^+$	$[\text{Gua}+\text{H}]^+$	114.8 (2.9)	120.9	4.9 (0.1)	119.7 (2.9)	125.8	10.3 (1.7)	109.4 (3.4)	115.5
	$[\text{Guo-Gua}+\text{H}]^+$	193.9 (5.8)	178.8	0.6 (3.0)	194.5 (6.5)	179.4	55.2 (11.0)	139.3 (12.8)	124.2

<sup>a</sup>Present results, uncertainties are listed in parentheses. <sup>b</sup>Values from the theoretical calculations at the B3LYP/6-311+G(2d,2p) level of theory using the B3LYP/6-311+G(d,p) optimized geometries.

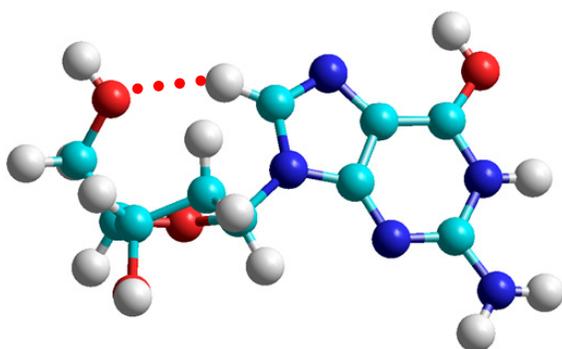
## Figure S1.



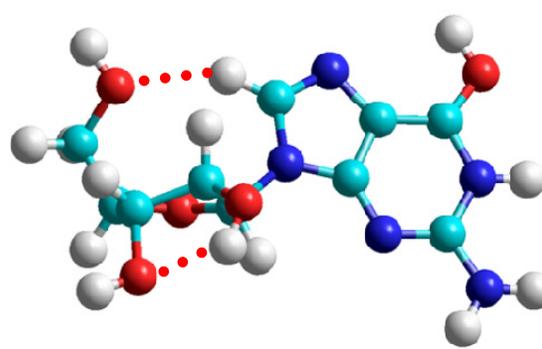
N7, anti, C3'-endo  
0.0, 0.0 kJ/mol



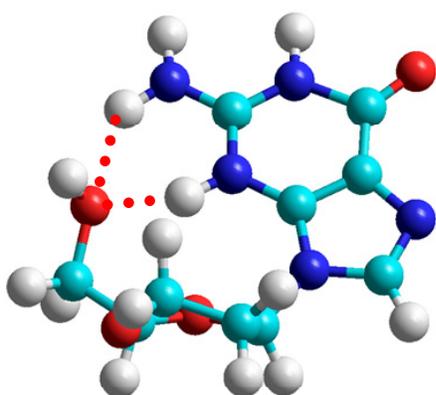
N7, anti, C3'-endo  
0.0, 0.0 kJ/mol



O6, anti, C2'-endo  
39.0, 37.5 kJ/mol

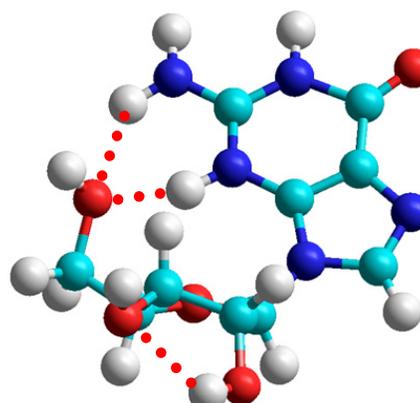


O6, anti, C2'-endo  
35.0, 35.2 kJ/mol



N3, syn, C3'-endo  
52.4, 40.9 kJ/mol

[dGuo+H]<sup>+</sup>



N3, syn, C3'-endo  
41.2, 40.1 kJ/mol

[Guo+H]<sup>+</sup>

**Figure S1.** The most stable N7, O6, and N3 protonated structures of [dGuo+H]<sup>+</sup> and [Guo+H]<sup>+</sup> optimized at the B3LYP/6-311+G(d,p) level of theory with the B3LYP/6-311+G(2d,2p) and MP2(full)/6-311+G(2d,2p) relative stabilities at 0 K shown in blue and red, respectively.