Supplemental Material

Electron Detachment Dynamics of the Iodide-Guanine Cluster: Does Ionization Occur from the Iodide or from Guanine?

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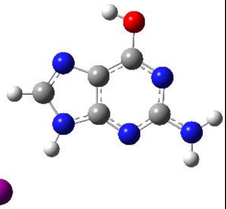
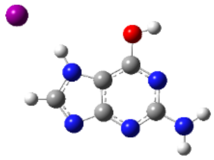
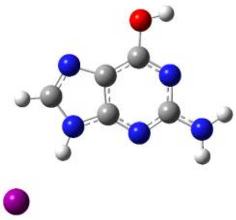
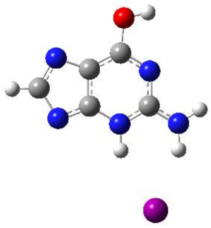
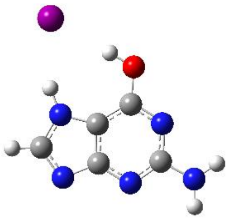
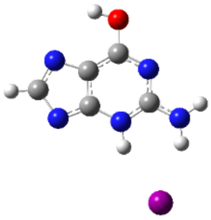
S1 Lowest Energy I^-·G clusters

The structures of I^-·G clusters were studied via DFT, at the B3LYP/6-311++G(2d,2p) level of theory on C, N, O, and H, and 6-311G(d,p) on I with the iodine core electrons being described using the Stuttgart/Dresden (SDD) electron core pseudopotential. 3H, 7H and 9H guanine isomers (with H on G3, G7 or G9) were investigated in their keto and enol tautomeric forms. The enolic forms were studied in their cis and trans isomeric forms (with respect to the $-NH_2$ group), as described in ref. S1. For each of these structures, different iodine positions near the nucleobase were calculated, and the lowest energy ones are shown in Table S1.

Table S1 Calculated structures of the I^-·G cluster. Calculations were performed were optimised at the B3LYP/6-311++G(2d,2p) level of theory on C, N, O, and H, and 6-311G(d,p)/SDD on I.

Structure	Relative Energy[a] (kJ/mol)	Structure	Relative Energy[a] (kJ/mol)	Structure	Relative Energy[a] (kJ/mol)
 I^-·G7	0	 I^-·G9_E_trans	25.0	 I^-·G7_E_cis	33.0
 I^-·G9	2.43	 I^-·G9_E_cis	28.7	 I^-·G3_E_cis	38.0
 I^-·G7_E_trans	3.45	 I^-·G3_E_trans	31.7	 I^-·G3	40.7

[a]Relative energies are zero point corrected energies.

S2 Collision Induced Dissociation

The fragments associated with ground-state thermal fragmentation were identified *via* collision-induced dissociation (CID) in the ion trap of the amaZon SL (Bruker, Daltoniks) [S2]. Here, selected molecular ions are trapped and accelerate to cause collisions with helium buffer gas and thus fragmentation. The acceleration is obtained by applying a voltage to the end-cap electrode, varying its amplitude between 0 and 10% (2.5 V being the maximum).

CID was performed on the isolated I^-·G cluster and the fragment production curves are shown in Figure S1.

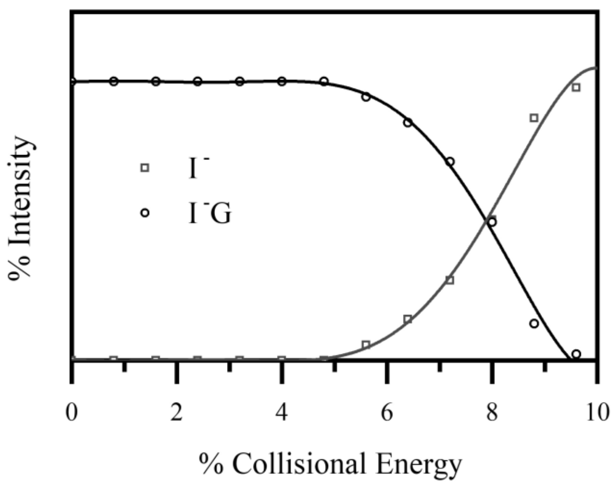


Figure S1. Fragment production curves for I^-·G upon CID between 0 and 10 % energy.

References

[S1] G. Chunga, H. Oh and D. Lee, J. Mol. Struct. THEOCHEM **730**, 241 (2005).

[S2] J.N. Louris, R.G. Cooks, J.E.P. Syka, P.E. Kelley, G.C. Stafford Jr. and J.F.J. Todd, Anal. Chem. **59**, 1677 (1987).