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SUPPORTING INFORMATION

A hitherto unknown stability of DNA basepairs

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I. COMPUTATIONAL DETAILS

A. Choice of methods

A simple practical approach for accomplishing the conventional Hermitian quantum chemical method for calculating energy position and reaction mechanism of a non-overlapping negative ion resonance (NIRS) is to adopt a standard bound state quantum chemical method using a *compact basis set*.[1,2] The basis set is chosen such that only one well separated discretized eigenfunction of the negative ion Hamiltonian uniquely describes the NIRS. Hence, computation of NIRS using such *compact basis sets of Gaussian functions* requires a particularly careful choice of the basis functions. Briefly, an approximation to the long-lived NIRS wavefunction of the basepair projected onto its many-electron interaction region is obtained as a single discrete eigenfunction of the electronic Hamiltonian of the basepair represented in the compact basis set. More importantly, the compact basis set approach enable us to conveniently study the reaction paths of NIRS using the conventional *ab initio* quantum chemical methods. Many NIRSs and their reactions have been characterized and studied using this approach.[3]

The interpair proton-transfer is in fact a stretching of a bond without causing any fragmentation of chemical bonds of the basepair. Since no bond-fragmentation is involved, simple ROHF-MP2 method is an ideal choice for computing the interpair proton-transfer reaction of NIRS using *compact basis set*. The use of ROHF-MP2 method provide us beautiful advantages in studying the chemical reaction mechanisms of one-particle NIRSs. Since the ROHF orbitals are optimized for the electron captured one-particle NIRSs, their chemistry can be conceptualized using the optimized molecular orbitals. The electron induced reaction is initiated because of the electron density relaxation due to resonance capture which is taken into account by the orbital relaxation at the ROHF level. The essential part of the electron correlation due to the electron attachment is also captured by the use of second order perturbation theory.

B. Choice of basis set

Pople's 6-311 split valence basis set is selected as the compact basis set because of two reasons: First, this basis set unambiguously yielded us the well isolated single discrete wavefunction corresponding to the Π^*-NIRS throughout the interpair proton transfer path. Second, it very well

captured the valence character of the Π^*-NIRS.

C. Computational studies

The geometries of the neutral basepairs are computed initially using a higher level basis set, where compact basis set is augmented with diffused set of functions. The dihedral angles of these initially computed geometries are retained in all the calculations reported in this work. The minimum energy paths (MEP) reported here are computed by relaxing all the coordinates and under the constraint that the dihedral planes of the target geometries are retained. The planarity of the neutral basepair is retained along the MEP because it avoid the collapse of the Π^*-NIRS wavefunction into localized σ^*-type NIRSs. The computed equilibrium geometry of the neutral basepairs from the minimum energy paths are given in Tables I-II.

By restricting the occupancy of the negative-ion electron in the π^*-orbital of one of the nucleobases of the basepair, the one-particle Π^*-NIRS of basepairs are prepared at the ROHF level. Using this ROHF wavefunction as zeroth-order reference wavefunction, the electronic energies, molecular geometries and the minimum energy path (MEP) corresponding to the interpair proton transfer are computed at the second order Møller-Plesset perturbation of electron-correlation. More specifically, the NIRS wavefunctions are computed initially for the proton transferred system i.e., for the points around *c* in the figures. This is an easy task because system at *c* is electronically more stable than the vertically electron attached neutral basepair (i.e., point *b*). This computed wavefunction of *c* is also used as initial guess for the immediate neighboring points around *c* in the minimum energy path. A maximum overlap is checked for the wavefunction from an SCF iteration step with the wavefunction from the previous iteration. This also help us to avoid the variation collapse of ROHF wavefunction. This process is repeated successively for all the points around *c* and the entire minimum energy path is thus constructed for a particular NIRS. In general, this simple approach using the compact basis set and RO-MP2 is powerful enough to describe the non-fragmenting chemical reactions of long-lived NIRSs with qualitative accuracy and provide valuable insights into their reaction mechanisms.

The electron attachment energy we have calculated for the basepair is scattered closely around the attachment energy of the isolated nucleobases reported in Ref. 4 and Ref. 5. This is very well

understandable because the NIRSs which we computed are simple one-particle π^* resonances (See Fig. S.4 for the π^* orbitals of negative ion resonance states). They are not originated due to electron correlation as in two-particle one-hole resonances. Moreover, unlike in Ref. 4 and Ref. 5, we have complementary neighboring base. It is also worth mention here that, due to the transfer of a partially positive charged hydrogen atom to the NIRS moiety, the basepair is electronically stabilized by the delocalization of negative charge over the entire basepair. This fact is also confirmed by the charge analysis.

TABLE I: The Cartesian coordinates of all atoms corresponding to the equilibrium neutral geometry of AT basepair. Units are in $\AA$.

N	4.9485526905	0.5728834628	0.1485936538
C	5.2324349284	-0.7891516951	0.1309765549
H	6.2349663318	-1.1789695799	0.2071746962
N	4.1246451720	-1.5441358037	-0.0114252060
C	3.0816453248	-0.5996169638	-0.1169986669
C	1.6761111544	-0.7769185435	-0.1059876708
N	1.0773838502	-1.9904958292	-0.2017322170
H	0.0661967753	-2.0609532492	-0.1049232040
H	1.6448262657	-2.8138337901	-0.0740225568
N	0.9070247717	0.3574704976	-0.1476502360
C	1.5030573572	1.5974717667	-0.0789159369
H	0.8264575716	2.4410200472	-0.1050867669
N	2.8300611171	1.8577022933	0.0117416933
C	3.5693443779	0.7075375144	0.0469002471
H	5.5964598602	1.3355789304	0.2667464595
C	-2.5501283721	-0.8754632952	0.0847782575
C	-4.0158542422	-0.8580567409	0.0789006537
C	-4.6373761156	0.3526469991	-0.0089005550
C	-2.5271588456	1.6092848319	0.0011212762
H	-5.7177093110	0.4491388840	-0.0364747043
O	-1.8707866061	-1.9507931019	0.0877343143
O	-1.8970198618	2.6923612463	-0.1048373617
N	-3.9261200771	1.5529397683	0.0468947067
H	-4.3936677937	2.4313429211	-0.1261788793
N	-1.9134636272	0.3676836691	0.1611873756
H	-0.8686837072	0.3642575454	0.0566733452
C	-4.7447266831	-2.1742000558	-0.0151014924
H	-4.4511101074	-2.7157146740	-0.9204008464
H	-4.5010880795	-2.8130987990	0.8398775136
H	-5.8278550444	-2.0613365693	-0.0373894259

TABLE II: The Cartesian coordinates of all atoms corresponding to the equilibrium neutral geometry of GC basepair. Units are in $\AA$.

N	-4.6611831146	-0.5679028487	0.0785533602
C	-4.9907788018	0.7892043998	0.1040255326
H	-6.0070362407	1.1435928034	0.1676290994
N	-3.9050681861	1.5766745166	0.0080274325
C	-2.8283830190	0.6706096923	-0.1117954174
C	-1.4170995137	0.9081047459	-0.0403232028
N	-0.6752920325	-0.2962613966	-0.1232191004
C	-1.2199159006	-1.5787031615	-0.0783332103
N	-2.5417209883	-1.8110125520	-0.0457431583
C	-3.2811580334	-0.6518438529	0.0044680367
H	-5.2784212040	-1.3557240656	0.1940582588
C	2.7729623502	1.3692369579	0.0180139780
C	4.2091364192	1.5366488190	-0.1155629486
C	4.9781726595	0.4101377625	-0.1584774345
C	2.9946384260	-1.0016040124	0.1157418685
H	6.0565742679	0.4307133429	-0.2601444852
O	2.5212464138	-2.1750491766	0.1745516233
N	4.3945049502	-0.8274697879	0.0310428219
H	4.9315387411	-1.6779499040	-0.0662144862
N	2.2161250885	0.1436844973	0.1865949370
H	0.3496971071	-0.1856161452	-0.0244305862
N	-0.3490852093	-2.6264244033	-0.1814257360
H	0.6509081251	-2.5036584418	-0.0320789667
H	-0.7489474008	-3.5392966320	-0.0369167380
O	-0.8106590190	2.0256977766	0.0102290993
N	1.9602939173	2.4427287846	0.0860729563
H	2.3186696601	3.3622000580	-0.1192700944
H	0.9194242412	2.3047029539	0.0923329653
H	4.6455657255	2.5143421337	-0.2795214560

1. The resonance capture of vLEE by the guanine moiety of GC basepair

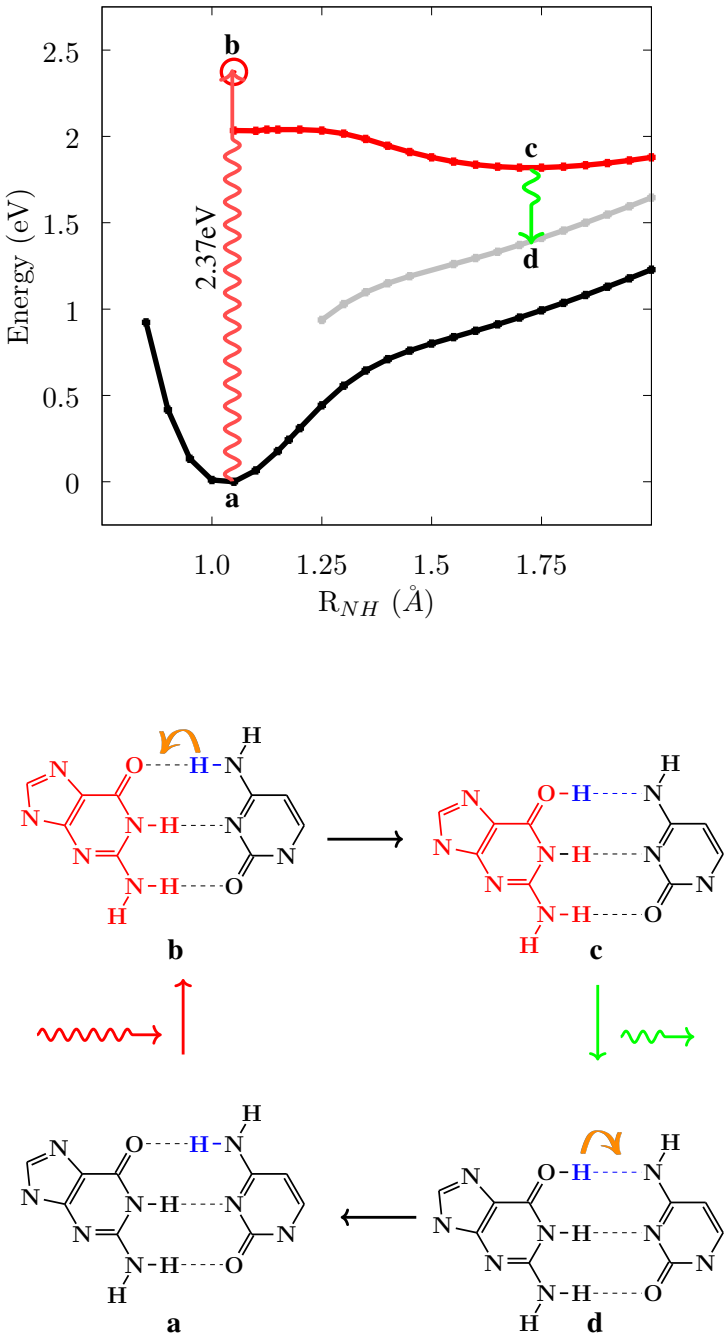

FIG. S1: The resonant capture of a vLEE by the guanine moiety of GC basepair and its subsequent autodetachment due to the temporary abstraction of an interpair proton from the cytosine moiety are illustrated (see Fig. 1 and the discussion on Pages 2-3 in the Communication).

In Fig. S1, we illustrate an identical molecular mechanism that protects the structural integrity of GC basepair after a vLEE of energy 2.37 eV is resonantly attached to its guanine moiety. The apparent similarity between Fig. 1 and Fig. S1, therefore, draw a general conclusion: In the case of resonance capture of vLEE by a purine base, i.e., guanine or adenine, its complementary base reversibly and rapidly transfer an interpair proton to metastabilize the resulting electron captured NIRS moiety, and the harmful excess electron is autodetached from its resulting metastable minimum of the basepair. It is also worth mention here that, Fig. 1 and Fig. S1 tend to reveal a very shallow minimum in the Frank-Condon region on the MEP of the NIRS. If the biochemical environment stabilizes and further deepens these minima, the vLEE can autodetach almost elastically, i.e., without inducing any structural changes in DNA. Future studies should, therefore, assess how the biochemical environment stabilizes these not so well developed minima.

2. *The resonance capture of vLEE by the thymine moiety of AT basepair*

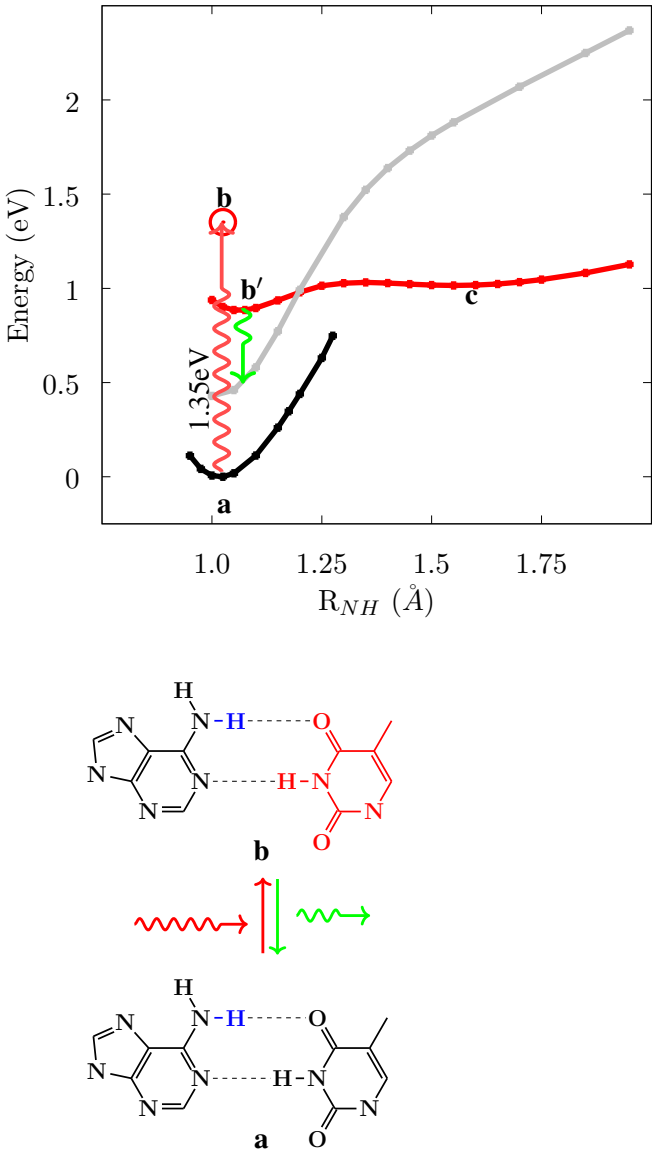

FIG. S2: The resonance capture of vLEE by the thymine moiety of AT basepair and subsequent autodetachment of the electron are illustrated (see Fig. 2 and the discussion on Pages 3-4 in the Communication).

3. The resonant capture of a vLEE by the cytosine moiety of GC basepair

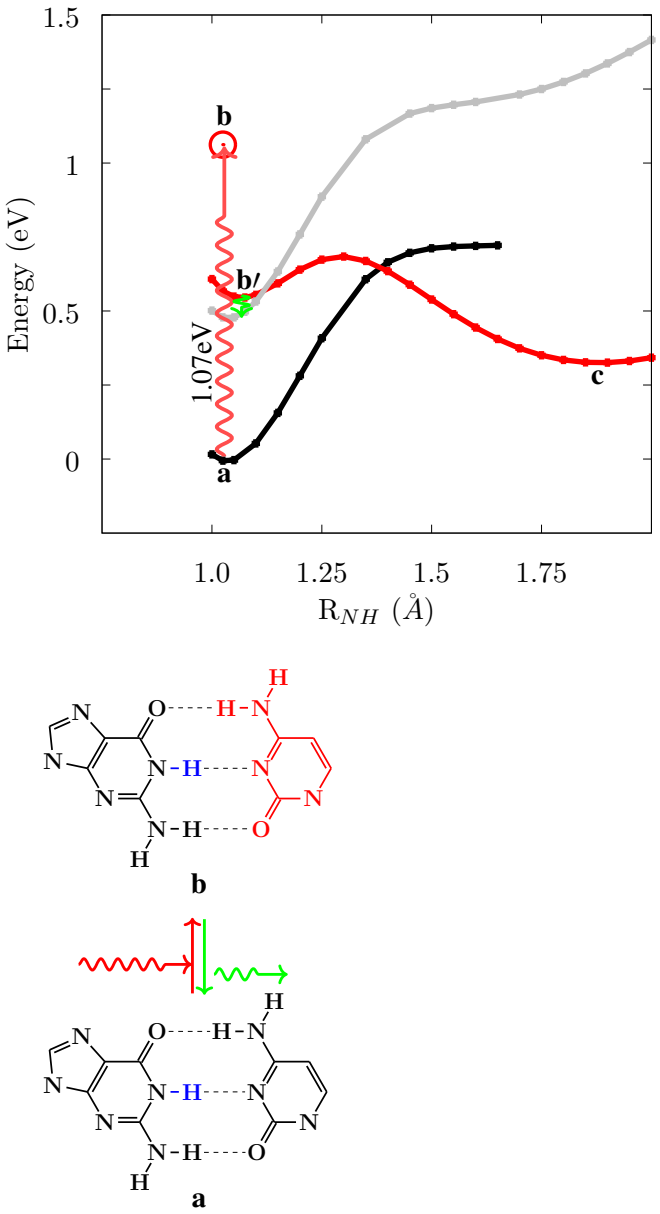

FIG. S3: The resonant capture of a vLEE by the cytosine moiety of GC basepair and its subsequent autodetachment are illustrated (see the text and the caption of Fig. 1). Unlike in Fig. 1, a metastable minimum (**b**′) is created in the Frank-Condon region itself due to the partial transfer of an interpair proton and the attached vLEE is autodetached from this metastable minimum.

4. The π^* orbitals of negative ion resonance states

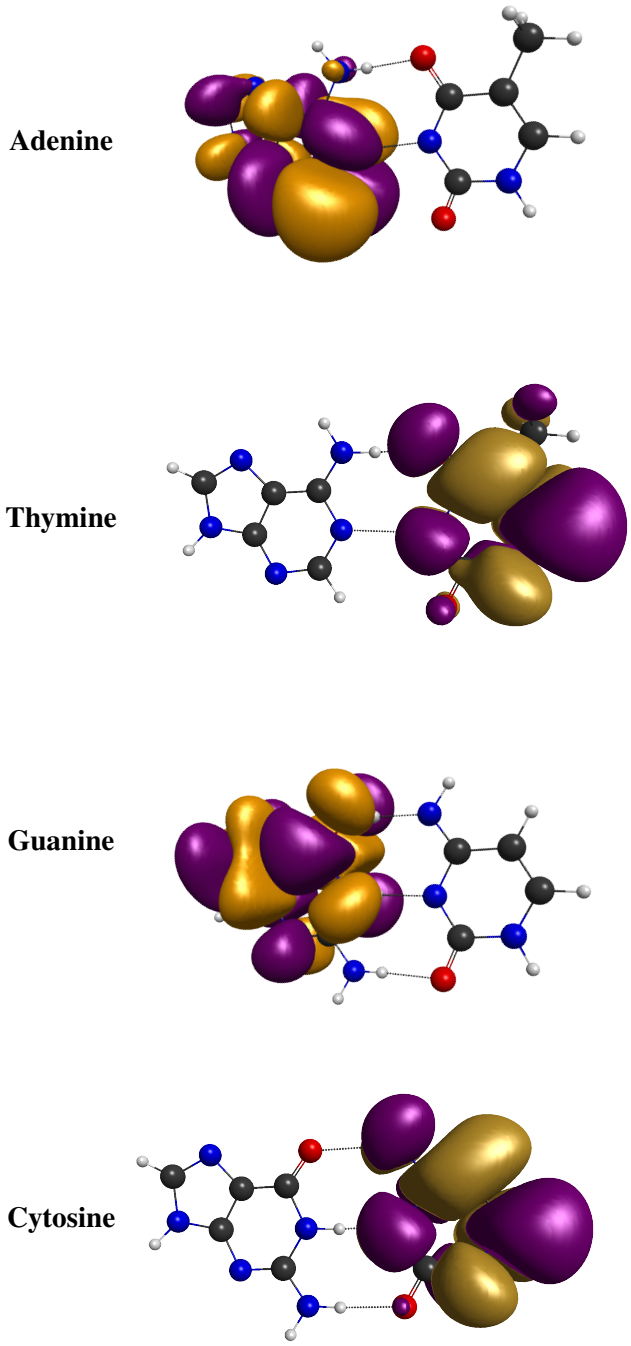

FIG. S4: The π^*orbitals corresponding to the point *c* in the Figs. 1-2 and Figs. S1-S2.

II. CHARGE BURIAL MECHANISM DUE TO THE BIOCHEMICAL ENVIRONMENT

If the metastable minimum of the NIRS is stabilized by the biochemical environment and becomes a bound anionic state, then a second possibility distinct from the autodetachment mechanism exists for the expulsion of the electron. In this case, the negative charge of the bound anionic state can be annihilated by a proton of the environment and subsequently create a negative charge elsewhere. A similar charge burial process is also known to occur when an excess electron is injected into the pyrimidine moieties.[6–8]

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