SUPPORTING INFORMATION

Ionization Dynamics of Aminopyridine Dimer: A Direct Ab-initio Molecular Dynamics (MD) Study

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1. Direct ab-initio MD calculation of $(AP)_2$ at 10 K.

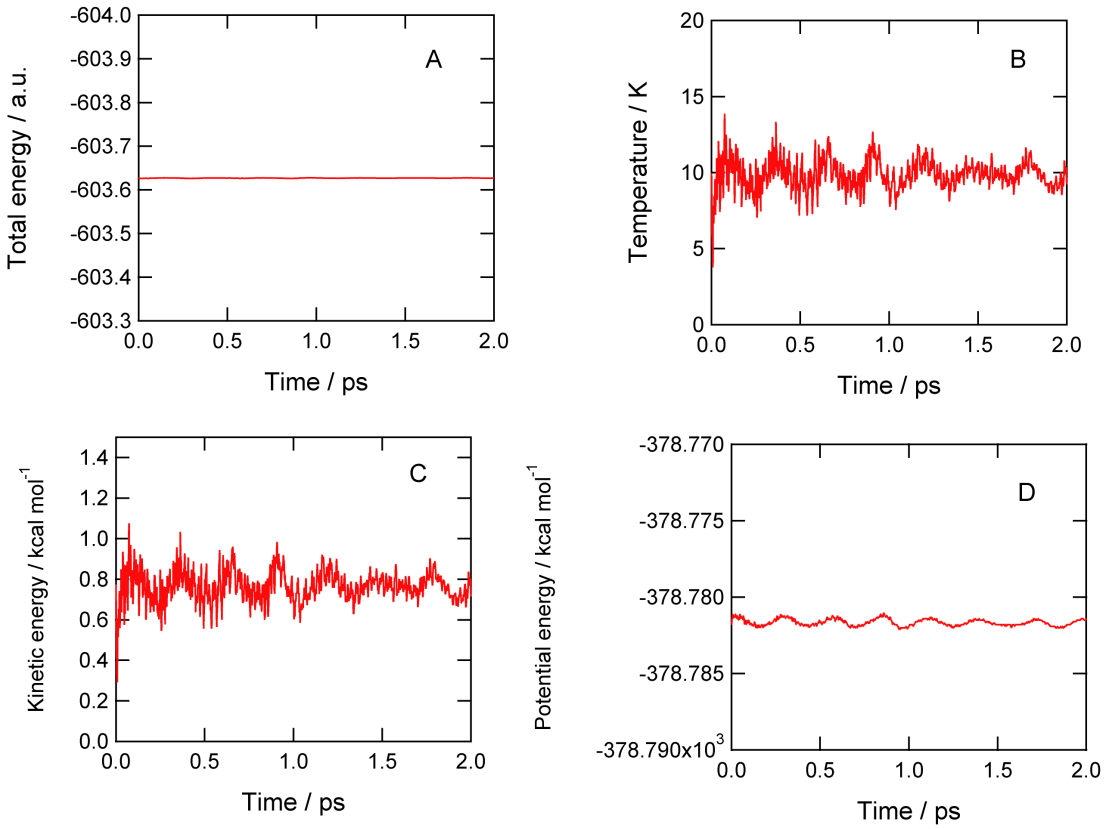

Figure S1. Result of direct ab-initio MD calculation of 2-aminopyridine dimer $(AP)_2$ at 10 K. Time profiles of (A) total energy, (B) temperature, (C) kinetic energy, and (D) potential energy.

2. Ionization dynamics of $(AP)_2$.

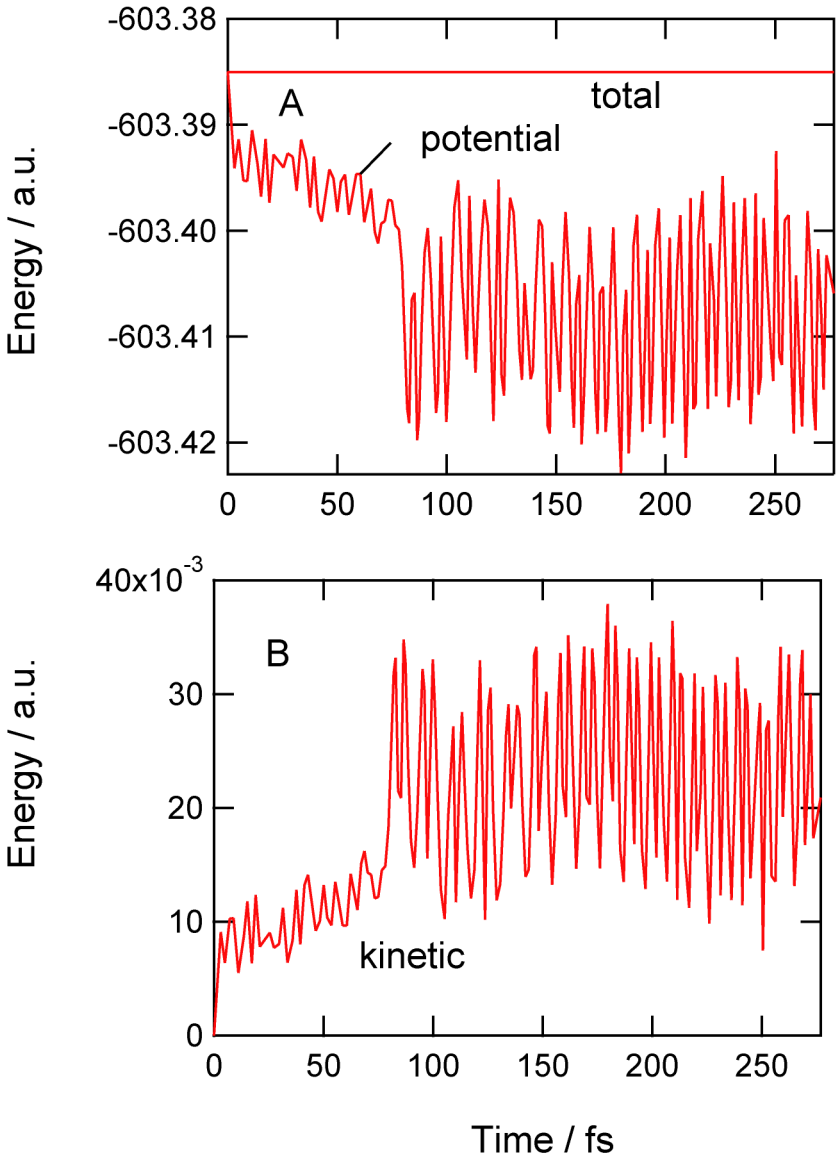

Figure S2. Time propagation of potential, kinetic and total energies of the ionization reaction of 2-aminopyridine dimer $(AP)_2$ obtained by direct ab-initio MD calculation.

3. Comparison of potential energies calculated by HF and MP2 methods.

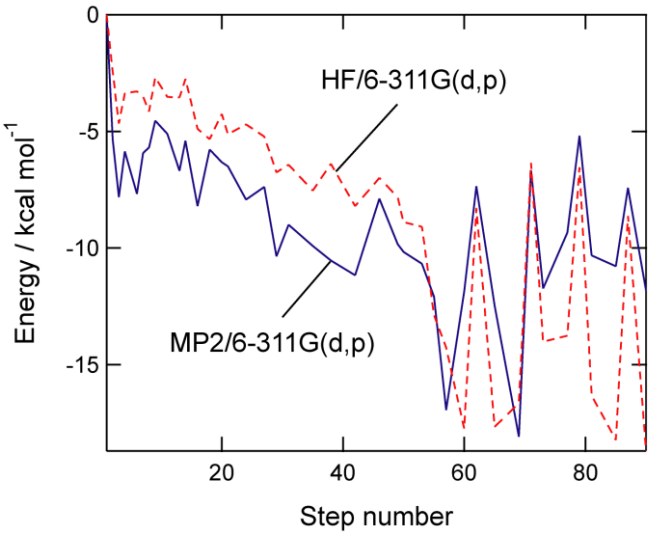

Figure S3. Time propagation of potential energy of the ionization reaction of 2-aminopyridine dimer. Direct ab-initio MD calculation was carried out at the HF/6-311G(d,p) level.

4. Harmonic vibrational frequencies

Table S1. Harmonic vibrational frequencies of $(AP)_2^+$ (Cs).

	frequency / cm^{-1}					
$(AP)_2^+$ (Cs)						
HF	3906(a')	3716(a')	3645(a')	3513(a')	3400(a')	3383(a')
/6-311G(d,p)	3374(a')	3371(a')	3358(a')	3355(a')	3343(a')	3333(a')
	1861(a')	1846(a')	1829(a')	1726(a')	1641(a')	1630(a')
	1626(a')	1584(a')	1561(a')	1522(a')	1510(a')	1466(a')
	1429(a')	1402(a')	1350(a')	1331(a')	1273(a')	1264(a')
	1231(a')	1227(a')	1160(a')	1154(a')	1137(a'')	1105(a'')
	1105(a')	1086(a')	1070(a')	1041(a')	1029(a'')	1015(a'')

	1014(a'')	946(a'')	913(a')	898(a'')	881(a')	860(a'')
	814(a'')	808(a'')	793(a'')	738(a'')	706(a'')	680(a')
	661(a')	604(a')	594(a')	565(a'')	509(a')	504(a'')
	454(a')	445(a'')	424(a'')	405(a'')	225(a'')	210(a'')
	142(a')	104(a'')	80(a')	70(a')	44(a'')	22(a'')
B3LYP	3673(a')	3484(a')	3239(a')	3232(a')	3217(a')	3212(a')
/6-311++G(d,p)	3207(a')	3199(a')	3193(a')	3185(a')	3159(a')	2950(a')
	1729(a')	1713(a')	1677(a')	1588(a')	1582(a')	1555(a')
	1520(a')	1486(a')	1467(a')	1431(a')	1409(a')	1385(a')
	1368(a')	1359(a')	1300(a')	1284(a')	1196(a')	1186(a')
	1176(a')	1157(a')	1110(a')	1086(a')	1055(a'')	1051(a')
	1046(a')	1021(a'')	1013(a'')	1008(a')	991(?a)	990(?a)
	965(a'')	885(a'')	868(a'')	862(a')	853(a')	802(a'')
	790(a'')	761(a'')	736(a'')	724(a'')	696(a'')	641(a')
	632(a')	578(a')	561(a')	526(a'')	491(a')	485(a'')
	431(a')	404(a'')	396(a'')	381(a'')	209(a'')	187(a'')
	164(a')	101(a'')	90(a')	87(a')	44(a'')	22(a'')

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5. Optimized Structure of $(AP)_2$

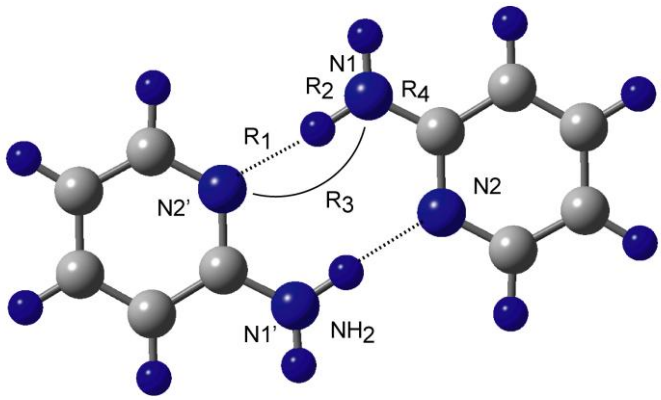

Table S2. Optimized geometries of $(AP)_2$ and $(AP)_2^+$ calculated at the HF/6-311G(d,p), MP2/6-311G(d,p) and B3PW91/6-311G(d,p) level. The bond distances are in A.

$(AP)_2$	parameter	HF	MP2	B3PW91
	R_1	2.204	1.997	1.965
	R_2	0.999	1.021	1.026
	R_3	2.204	1.997	1.965
	R_2'	0989	1.004	1.003
$(AP)_2^+$	parameter	HF	MP2	B3PW91
	R_1	1.013	1.054	1.051
	R_2	1.982	1.749	1.783
	R_3	2.092	1.937	1.921
	R_2'	1.006	1.020	1.020

6. Ionization dynamics of AP-$(H_2O)_2$ complex

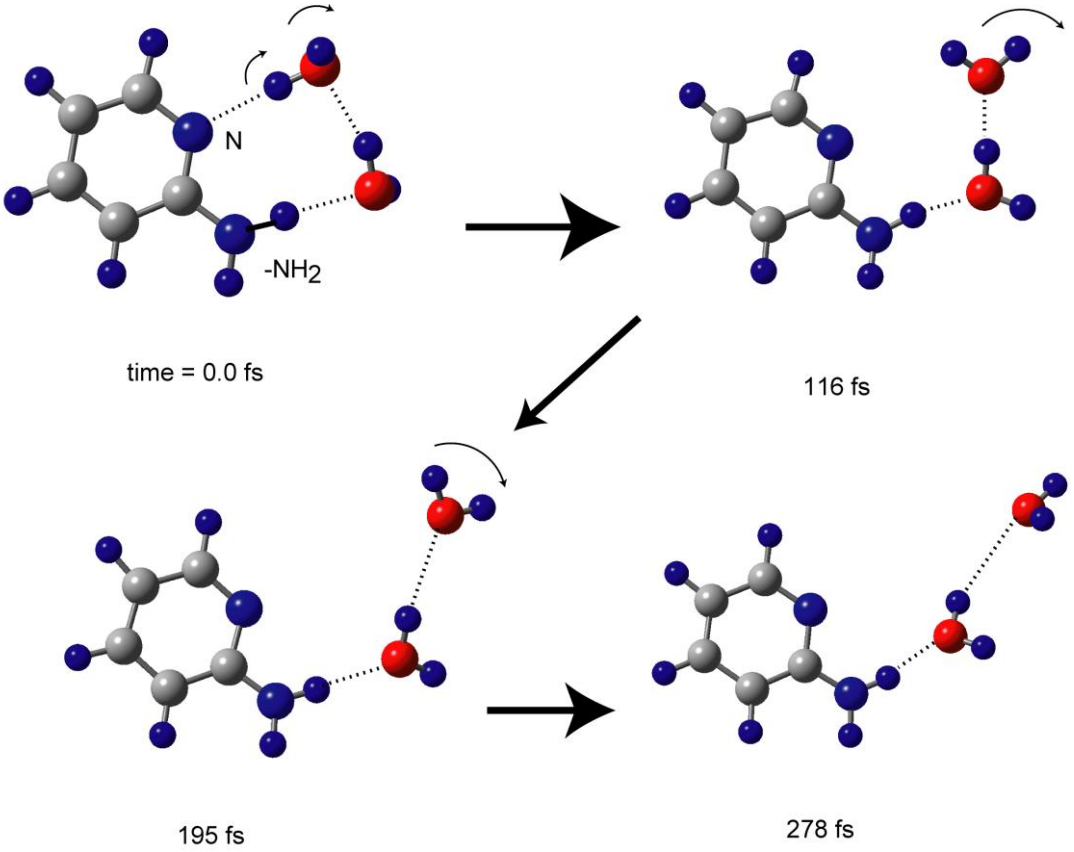

Figure S4. Snapshots of the ionization reaction of hydrated 2-aminopyridine dimer. Direct ab-initio MD calculation was carried out at the HF/6-311G(d,p) level.

7. Energy diagram of the proton transfer reaction

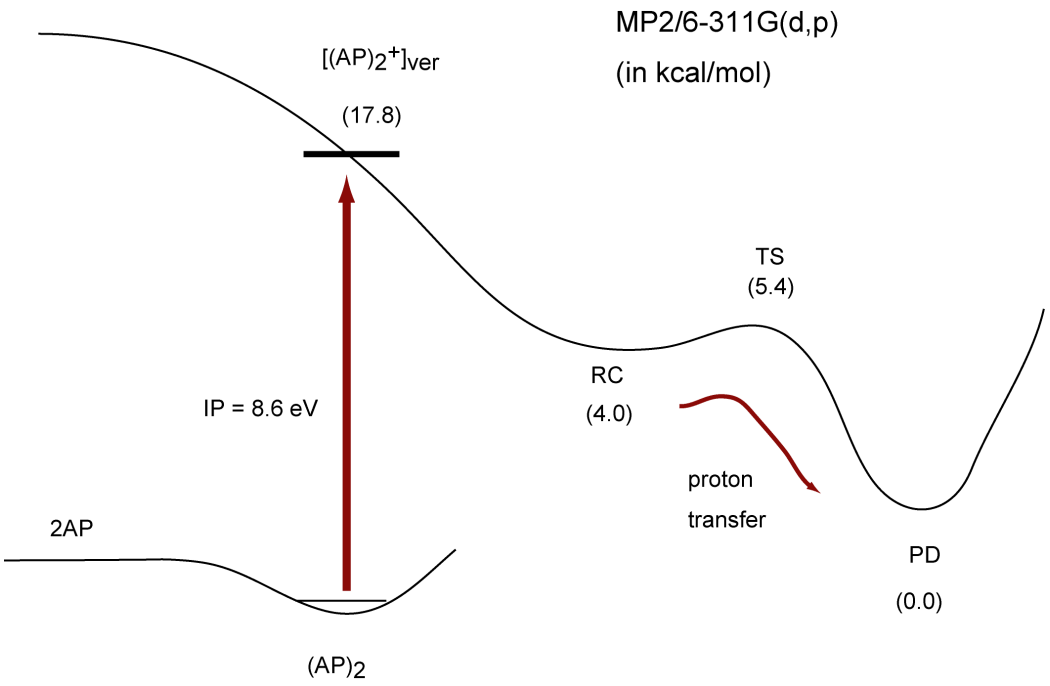

Figure S5. Potential energy diagram of the ionization reaction of 2-aminopyridine dimer calculated at the MP2/6-311G(d,p) level.

8. HOMO and LUMO of $(AP)_2$, $[(AP)_2^+]_{ver}$ and PD

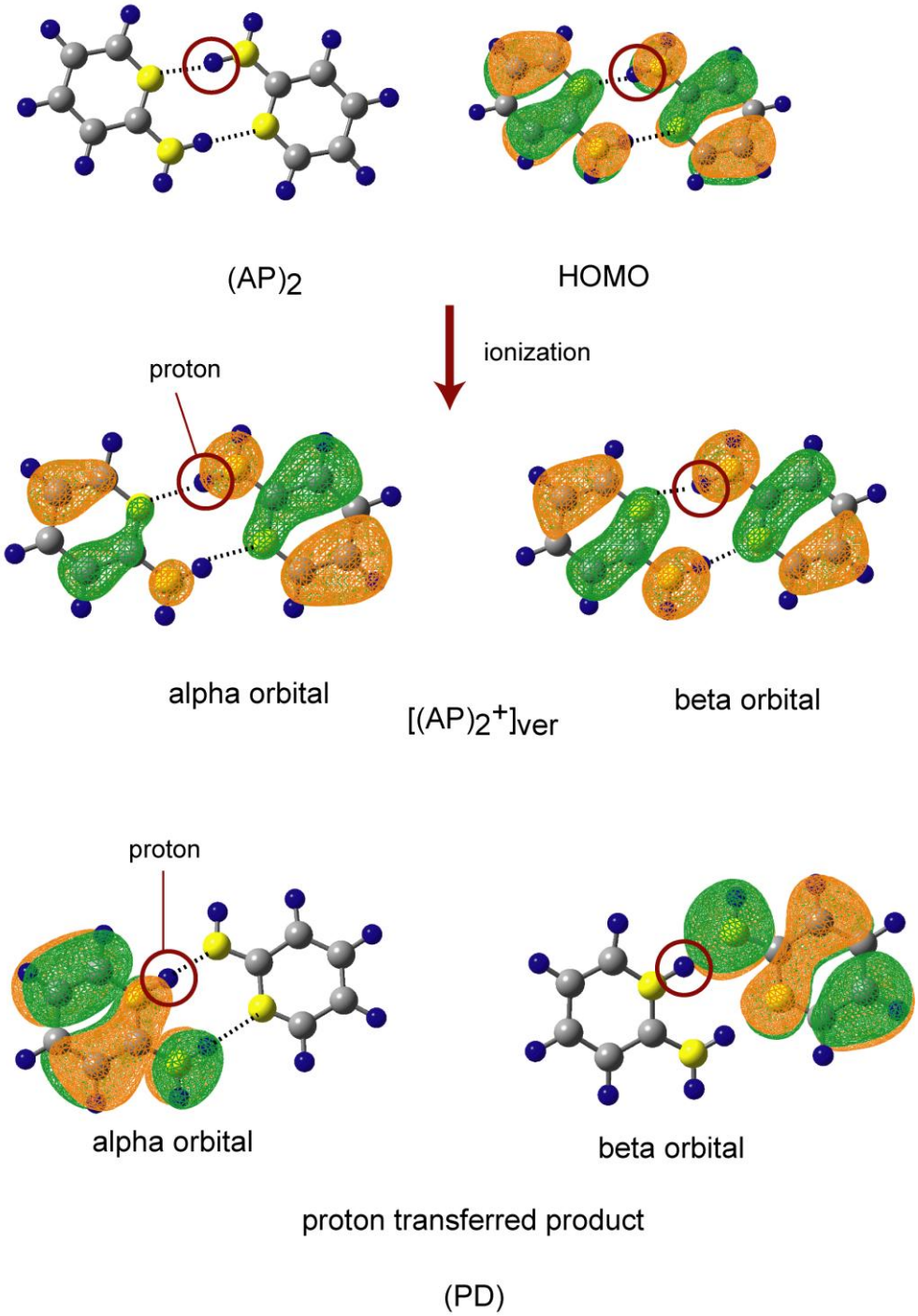

Figure S6. Illustrations of highest occupied molecular orbital, alpha- and beta- orbitals.

9. NPA atomic charges

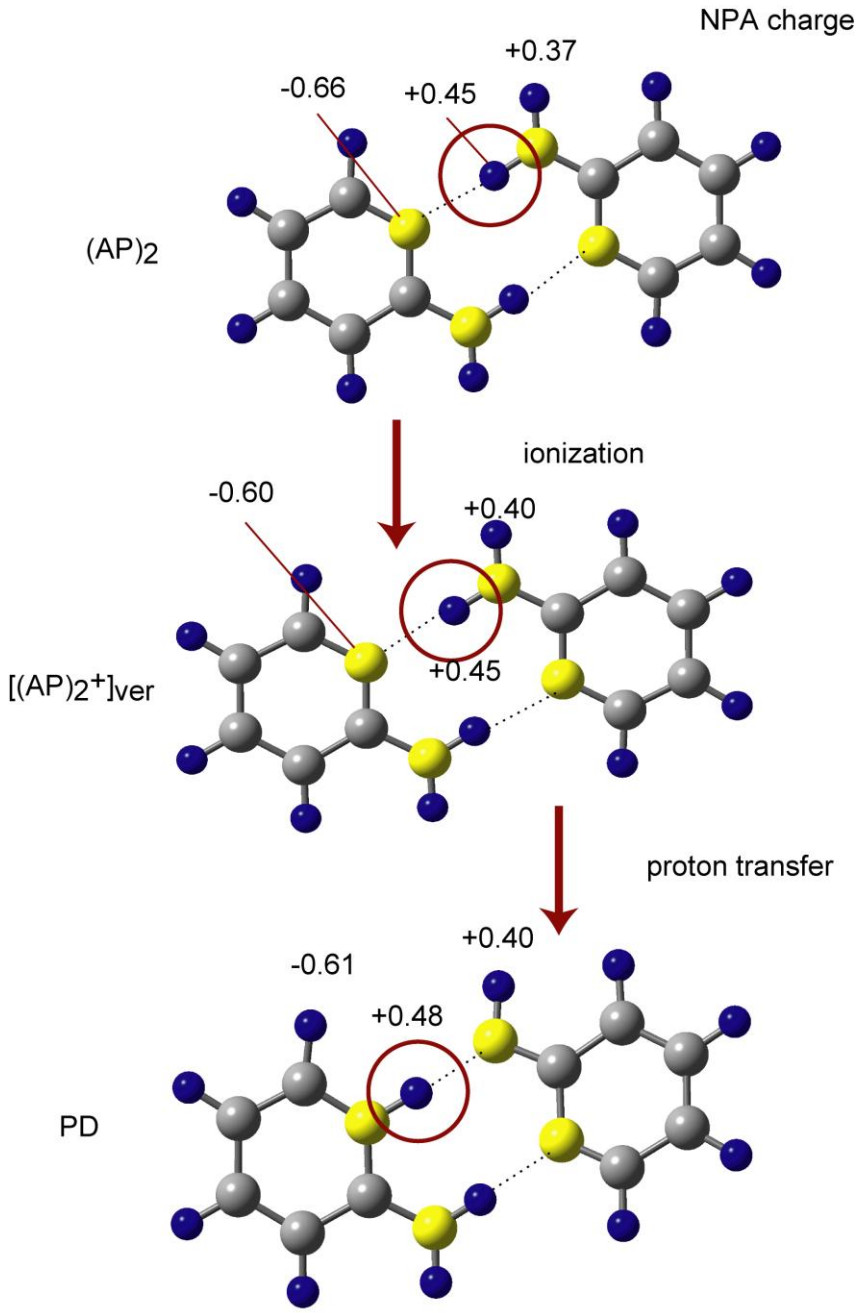

Figure S7. NPA atomic charges calculated at the MP2/6-311G(d,p) level.