Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Nonadiabatic Dynamics of Floppy Hydrogen Bonded Complexes: Case of Ionized Ammonia Dimer

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1 Cartesian coordinates

Geometries of monomers and dimers were optimized in Gaussian 09 using the MP2/aug-cc-pVTZ method. For transition state search, we used the QST3 approach. All coordinates are in Ångström units. We further add the ground state structures of the ionized ammonia dimer calculated at the EOM-IP-CCSD level with 6-311++g(d,p) basis using Q-chem code.

Ammonia monomer

Neutral

E(HF)= -56.2201009 a.u.. *E*(MP2)= -56.4605215 a.u.

N	0.000000	0.000000	0.000000
H	0.000000	0.000000	1.014867
H	0.973569	0.000000	-0.286561
H	-0.383065	0.895041	-0.286564

Ionized

E(HF)= -55.9035555 a.u.. *E*(MP2)= -56.0840433a.u.

N	0.000000	0.000000	0.000000
H	0.000000	0.000000	1.023019
H	0.886073	0.000000	-0.511300
H	-0.885691	-0.000035	-0.511977

Neutral ammonia dimer

Cyclic structure

E(HF)= -112.4428799 a.u.. *E*(MP2)= -112.926244 a.u.

N	-0.109280	-0.000130	-0.093054
N	-0.007446	-0.002420	3.072990
H	0.597882	0.003198	0.634013

H	0.065589	-0.810146	-0.674572
H	0.056435	0.812863	-0.673096
H	-0.713904	-0.005747	2.345234
H	-0.173720	-0.815408	3.652879
H	-0.182870	0.807597	3.654340

Eclipsed structure (GS)

E(HF)= -112.4430238 a.u.. *E*(MP2)=- -112.9263185 a.u.

N	-0.000695	0.000311	-0.000185
N	0.000152	-0.002643	3.234007
H	0.983819	0.003894	0.238874
H	-0.157508	-0.812108	-0.583664
H	-0.163782	0.812561	-0.582177
H	-0.298108	-0.002907	2.262376
H	-0.412466	-0.815486	3.674011
H	-0.418727	0.806185	3.675493

Ionized ammonia dimer

Proton-transferred structure (PT)

E(HF)= -112.1825628 a.u.. *E*(MP2)= -112.6087265 a.u.

N	0.093792	-0.075180	-0.280404
N	-0.029163	0.077704	2.480220
H	1.022072	0.191680	-0.605058
H	-0.100388	-1.026923	-0.588248
H	-0.593464	0.551439	-0.696733
H	0.046189	-0.016298	0.789943
H	-0.384327	-0.632236	3.120907
H	0.272082	0.856514	3.066227

Head-to-head structure (HH)

E(HF)= -112.154695 a.u.. *E*(MP2)= -112.6015826 a.u.

N	0.069214	-0.080544	-0.173594
N	0.001214	0.059245	1.983667
H	1.010753	-0.379136	-0.397247
H	-0.634028	-0.764791	-0.424498
H	-0.143230	0.849474	-0.513597
H	-0.940088	0.358653	2.207218
H	0.212649	-0.871154	2.323240
H	0.705082	0.742691	2.234980

Proton-transferred structure (PT)

E(EOM-IP-CCSD/6-311++G(d,p)) = -112.5986993360 a.u.

N	-1.30408694	0.00002115	0.00014138
N	1.45520713	-0.00001245	-0.00033993
H	-1.65791090	0.78542069	-0.54873498
H	-1.65775941	-0.86743499	-0.40693655
H	-1.65876223	0.08172156	0.95459053
H	-0.23398842	0.00013478	0.00054359
H	2.07536376	-0.81623477	0.00140200
H	2.07521587	0.81632962	0.00047875

Head-to-head structure (HH)

E(EOM-IP-CCSD/6-311++G(d,p)) = -112.5918681083 a.u.

N	0.00000003	-0.00000001	1.10408753
N	-0.00000002	-0.00000001	-1.10408755
H	0.00077386	0.97711675	1.38024879
H	-0.84659470	-0.48788824	1.38024911
H	0.84582113	-0.48922841	1.38024876
H	-0.00073448	-0.97711678	-1.38024890
H	-0.84584091	0.48919432	-1.38024850
H	0.84657499	0.48792241	-1.38024922

Transition state structure (TS)

E(HF)=-112.1512334 a.u.. *E*(MP2)=-112.5804216

N	0.069613	-0.092743	-0.379569
N	0.089604	0.037770	2.186072
H	0.992357	-0.440991	-0.619429
H	-0.596424	-0.729395	-0.807984
H	-0.033966	0.798073	-0.856726
H	-0.634911	0.168086	1.478998
H	0.326297	-0.900471	2.491898
H	0.721445	0.802292	2.400888

Fig. 1: Transition state geometry of the ionized ammonia dimer optimized at the MP2/aug-cc-pVTZ level of theory.

Tab. 1: Optimized geometry parameters of the ionized ammonia dimer (in Å units).

Method/aug-cc-pVTZ	**PT**		**HH**	**TS**	
	N_2H_6	*NN*	*NN*	N_1H_6	*NN*
HTCH407	1.68	2.77	2.33	-	-
B97D	1.64	2.75	2.31	-	-
B3LYP	1.69	2.77	2.28	1.81	2.68
BHandHLYP	1.72	2.78	2.21	1.93	2.61
MP2	1.69	2.77	2.16	2.00	2.57
CCSD	1.73	2.79	2.18	-	-
EOM-IP-CCSD[a]	1.69	2.76	2.21	-	-

a) Optimized with 6-311++g(d,p) basis.

2 Population analyses

Tab. 2: The population analyses of neutral (GS) and ionized structures of ammonia dimer calculated at the MP2/aug-cc-pVTZ level. The charges are shown in the units of the elementary charge *e*. Acronym FC stands for the Franck−Condon point (i.e. the vertically ionized ammonia dimer), PT for proton transferred, TS for transition state and HH for head-to-head structure.

Type of charge	GS	FC	PT	TS	HH
Hbond−acceptor					
Mulliken	0.01	0.08	0.84	0.10	0.50
NBO	0.01	0.03	0.89	0.12	0.50
MK	0.07	0.09	0.84	0.10	0.50
Hbond−donor					
Mulliken	−0.01	0.92	0.16	0.90	0.50
NBO	−0.01	0.97	0.11	0.88	0.50
MK	−0.07	0.91	0.16	0.90	0.50

The calculated charges well agree with Hahn and Lee work.[1]

3 Further potential energy scans

Linear interpolation between the Franck-Condon point (i.e. ionized ammonia dimer in its eclipsed geometry) and global minima on the ionized PES calculated at the CASSCF(11/6) level with 6-31++G(d.p) basis set. Results are very close to the MRCI(11/6)/aug-cc-pVTZ (see Fig. 4 below) and benchmark EOM-IP-CCSD/aug-cc-pVTZ calculations (see the main text).

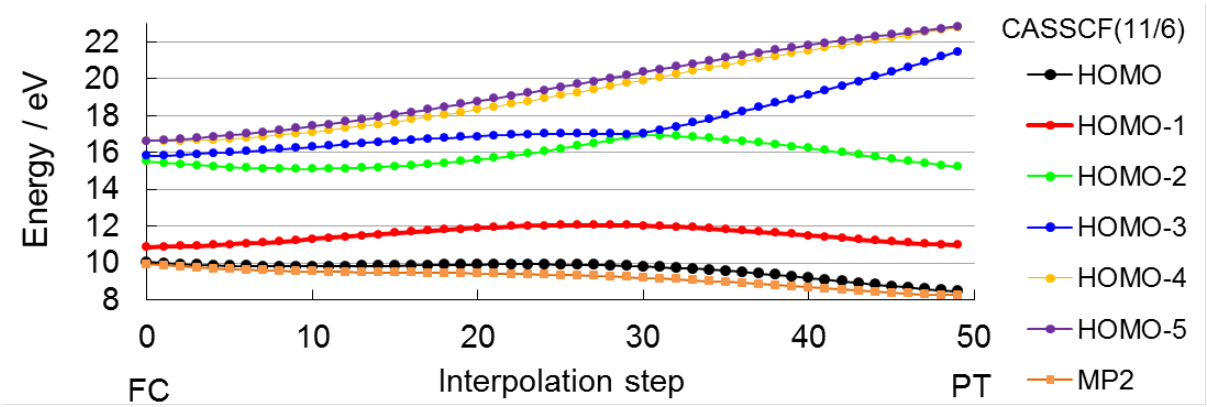

Fig. 2: Ionization energies of ammonia dimer along the proton transfer channel at the MP2 and CASSCF(11/6) level of theory with 6-31++G(d.p) basis set.

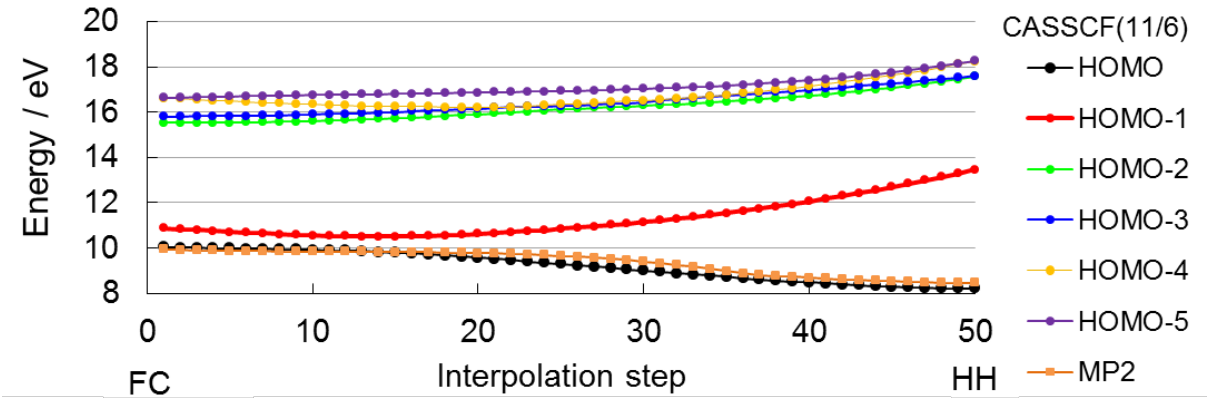

Fig. 3: Ionization energies of ammonia dimer along the FC→HH channel at the MP2 and CASSCF(11/6) level of theory with 6-31++G(d.p) basis set.

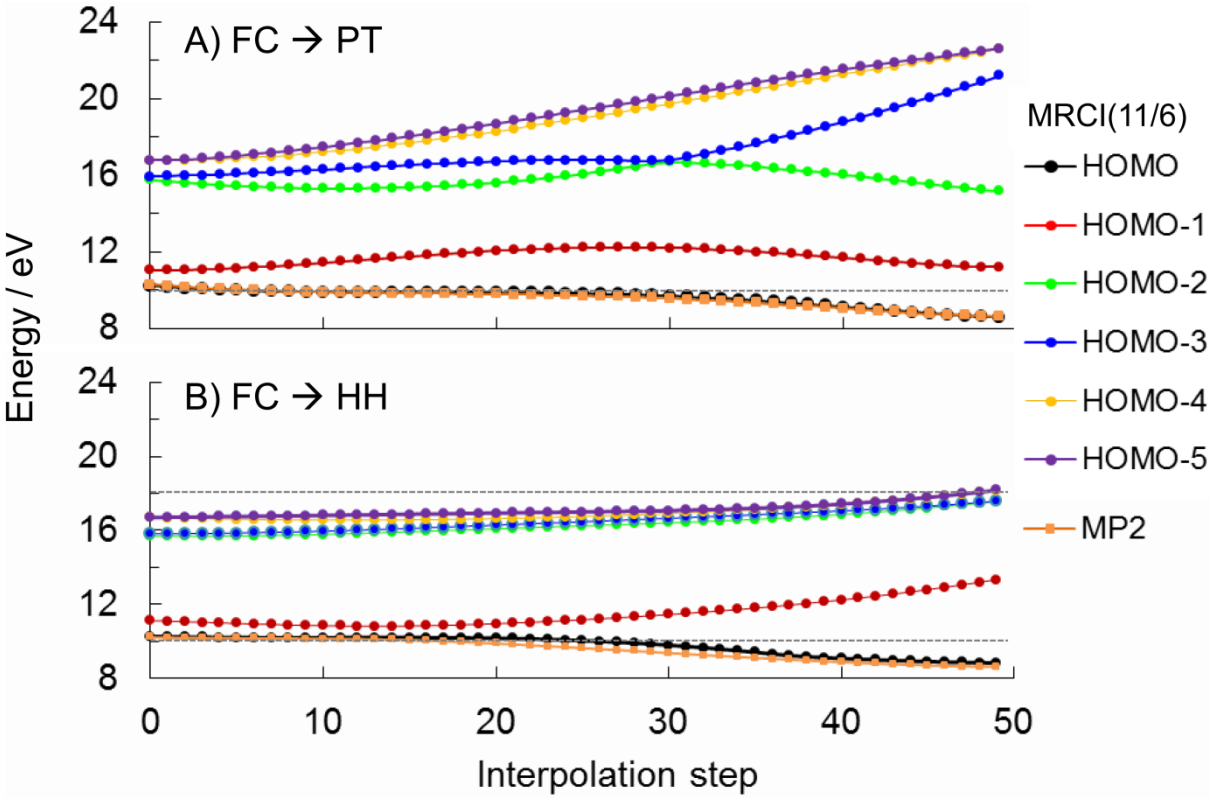

Fig. 4: Potential energies of ionized ammonia dimer along interpolation coordinates connecting neutral ground state optimal structure (FC point) and two minima on the ionized state PES. Energies were calculated at MP2 and MRCI(11/6) level of theory with aug-cc-pVTZ basis set. The energies are shown relatively to the ground state minimum of neutral ammonia dimer.

Similarly, PES scan at the MRCI(11,6)/6-31++G(d,p) level of theory along the hydrogen bonding parameters well agree with the EOM-IP-CCSD scan.

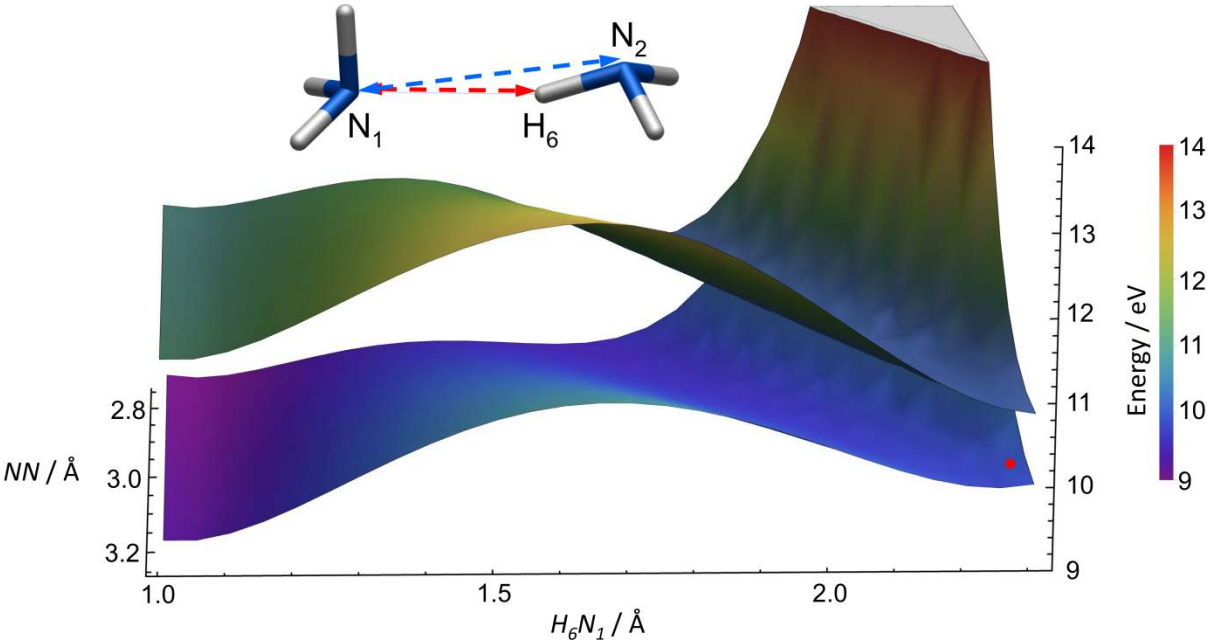

Fig. 4: Potential energy surfaces of the ammonia dimer as a function of the hydrogen bond length (N_1H_6) and intermolecular distance (N_1N_6) for the ground (lower PES) and the first excited (higher PES) states of ionized ammonia dimer calculated at the MRCI(11,6)/6-31++G(d,p) level of theory. The energies are shown relatively to the ground state minimum of neutral ammonia dimer.

4 Note on performance of DFT methods for ionized dimers

It was shown before that using DFT for calculations of (non)symmetrical radical-cations can leads to spurious effects due to the self-interaction error (SIE).[2] This is typical problem for the three-electron bond in the HH structure with delocalized charge between NH_3 units. Similar problem was found before in the DFT calculations in many other system, e.g. in the first-row isoelectronic ionized water and hydrogen fluoride dimers, mixed water-ammonia dimer or similarly in inert gas ionized dimers such as $He_2^{\cdot+}$ and $Ne_2^{\cdot+}$.[1, 3-5] Hybrid B3LYP functional also fails. The problem can be suppressed by including higher fraction of the exact exchange into the functional, e.g. within the BHandHLYP functional. As already noticed, the activation energy of $\mathrm{PT} \rightarrow \mathrm{HH}$ reaction through transition state is 0.70 eV at the CCSD(T)/aug-cc-pVTZ level while in the worst performing DFT B3LYP/aug-cc-pVTZ method is only 0.45 eV.

Also otherwise positive reaction energy is negative in this case. Energy at BHandHLYP/aug-cc-pVTZ level is 0.68 eV and reaction energy is positive.

References

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