Supporting Information

Comments on the accuracy of energetics (vertical excitation energy with the same geometry and energy difference with different geometries)

Table 1 Summary of energy (in a.u.) for NH_3 at equilibrium and D_{3h} conical intersection geometries.

	$E(S_0,\text{Equilibrium})^a$	$E(S_1,FC)$	$E(CI)$	$\Delta E(S_1\text{-}S_0,FC)$	$\Delta E(CI\text{-}S_0)$	$\Delta E(CI\text{-}S_1)$
pp-RPA-B3LYP	-56.779	-56.537	-56.477	0.242	0.302	0.060
pp-TDA-B3LYP	-56.776	-56.537	-56.479	0.239	0.297	0.058
SA-CASSCF[b]	-56.234	-56.026	-55.970	0.208	0.264	0.056
CASSCF	-56.188	-56.038	-55.970	0.150	0.218	0.068
(EOM)CCSD[c]	-56.420	-56.184		0.236		

a. For convenience, the equilibrium geometry for the ground state (or Frank-Condon (FC) point) is simply obtained from a B3LYP/aug-cc-pVDZ optimization.
b. State-averaged CASSCF, which equally averages over the lowest two states.
c. CCSD and EOM-CCSD results as a benchmark standard value for the vertical excitation at the equilibrium geometry. However, since it is a single reference method, it is not used to compute the energy for CI.

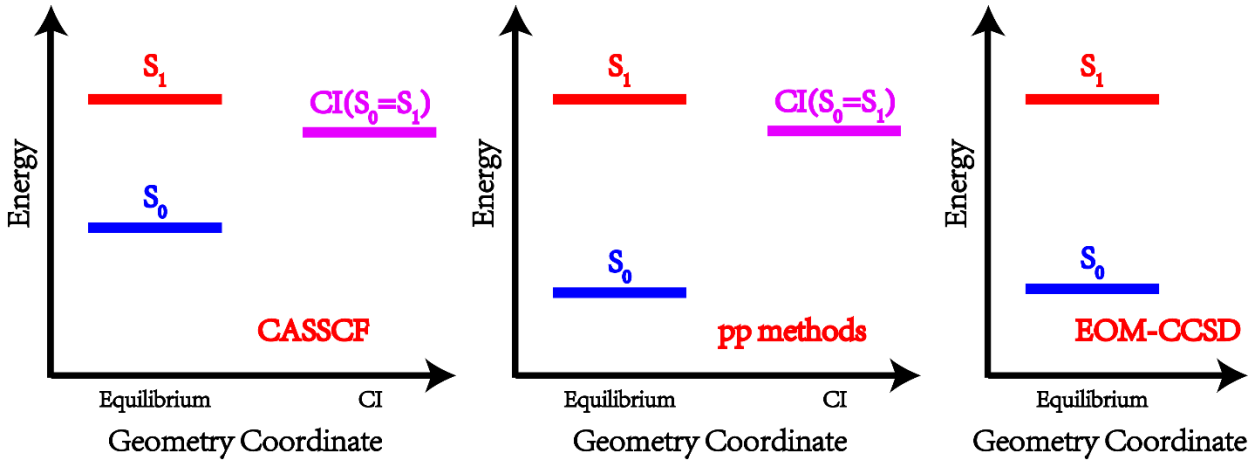

Figure 1 Sketch of the relative energies of S_1, S_0, and CI, with aligned S_1 energies for easy comparison

From Table 1 and Figure 1, we can see that

1. The pp methods give good vertical excitations at the equilibrium geometry. The CASSCF method partially suffers from the lack of dynamic correlation and has less accurate excitation results.
2. The pp methods and CASSCF well agree on $\Delta E(CI\text{-}S_1)$, which is the energy between their own conical intersection point and the FC point.
3. The pp methods and CASSCF do not agree well for $\Delta E(CI\text{-}S_0)$. It is possible that both the contracted orbitals for pp and the lack of dynamic correlation for CASSCF contribute to the discrepency. However, it is temporarily beyond the scope of current project, and it awaits further investigation.
4. In general, the pp methods perform well for the energy differences for NH_3.