Luning Zhao[1] and Eric Neuscamman[1,2,*]
[1] *Department of Chemistry, University of California, Berkeley, CA, 94720, USA*
[2] *Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720, USA*
(Dated: November 14, 2019)

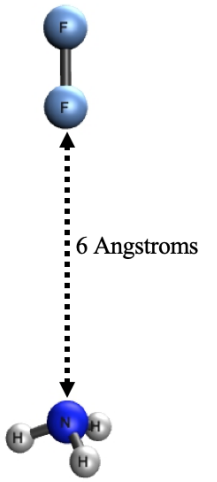

FIG. S1. Geometry of the NH_3-F_2 dimer. The N-H bond length and H-N-H bond angle is 1.02$\mathring{A}$ and 106.2°. The F_2 bond length is 1.43$\mathring{A}$.

I. MOLECULAR GEOMETRIES

In H_2O the H-O-H bond angle is chosen to be 104.5° and the O-H bond length is 0.96$\mathring{A}$. In CH_2O the H-C-H bond angle is 116°, and the C-H and C-O bond length are 1.11$\mathring{A}$ and 1.21$\mathring{A}$ respectively. In LiH the bond length is 1.6$\mathring{A}$, and the He-Be separation is 3.5$\mathring{A}$. The geometry of the NH_3-F_2 dimer is shown in Figure S1.

II. ABSOLUTE EXCITATION ENERGIES

The absolute excitation energies studied in this work is shown in Table I, II, III, and IV.

TABLE I. Excitation energies of DF-ESMF and EOM-CCSD for the system studied in eV. Note that the BHHLYP excitation energy of LiH $^3(\sigma \rightarrow \sigma^*)$ state is from the single-CSF formalism, and the corresponding excitation energy is 3.07eV if the multi-CSF formalism is used.

	LDA	B3LYP	BHHLYP	EOM-CCSD
H_2O $^1(n\rightarrow \pi^*)$	9.07	8.66	8.26	8.07
H_2O $^3(n\rightarrow \pi^*)$	8.23	7.86	7.50	7.39
LiH $^1(\sigma \rightarrow \sigma^*)$	4.62	4.23	3.60	3.47
LiH $^3(\sigma \rightarrow \sigma^*)$	4.47	4.12	3.50	3.09
CH_2O $^1(n\rightarrow \pi^*)$	4.57	4.51	4.13	4.13
CH_2O $^3(n\rightarrow \pi^*)$	3.85	3.86	3.57	3.64
CH_2O $^1(\pi \rightarrow \pi^*)$	9.94	9.71	8.93	10.08
CO $^1(\pi \rightarrow \pi^*)$	7.13	6.17	4.86	5.49
NH_3-F_2	10.59	10.12	9.03	9.29
Ne 2s→3s	42.16	43.24	44.56	47.30
Ne 2p→3p	22.36	21.69	20.79	20.04

TABLE II. Excitation energies of TDDFT for the system studied in eV.

	LDA	B3LYP	BHHLYP	ωB97X
H_2O $^1(n\rightarrow \pi^*)$	7.34	7.54	8.14	N/A
H_2O $^3(n\rightarrow \pi^*)$	6.70	6.82	7.36	N/A
LiH $^1(\sigma \rightarrow \sigma^*)$	3.16	3.34	3.65	N/A
LiH $^3(\sigma \rightarrow \sigma^*)$	2.64	2.74	3.00	N/A
CH_2O $^1(n\rightarrow \pi^*)$	3.81	4.02	4.18	N/A
CH_2O $^3(n\rightarrow \pi^*)$	3.13	3.29	3.43	N/A
CH_2O $^1(\pi \rightarrow \pi^*)$	9.23	9.63	10.12	N/A
CO $^1(\pi \rightarrow \pi^*)$	5.52	5.21	4.99	N/A
NH_3-F_2	0.00	1.88	5.32	5.84
Ne 2s→3s	39.09	41.23	44.36	41.95
Ne 2p→3p	17.78	18.27	19.60	N/A

TABLE III. Excitation energies of ROKS for the system studied in eV.

	LDA	B3LYP	BHHLYP	ωB97X
H_2O $^1(n\rightarrow \pi^*)$	8.15	7.82	7.79	N/A
LiH $^1(\sigma \rightarrow \sigma^*)$	3.48	3.41	3.37	N/A
CH_2O $^1(n\rightarrow \pi^*)$	3.94	3.79	3.68	N/A
NH_3-F_2	3.80	3.77	4.04	4.06

TABLE IV. Excitation energies of ΔSCF-DFT for the system studied in eV.

	LDA	B3LYP	BHHLYP	ωB97X
CH_2O $^1(\pi \rightarrow \pi^*)$	9.38	9.55	8.03	N/A
CO $^1(\pi \rightarrow \pi^*)$	5.64	3.26	0.00	N/A
NH_3-F_2	9.45	9.06	8.38	9.10
Ne 2s→3s	41.18	42.57	44.36	43.15
Ne 2p→3p	20.31	19.73	19.58	N/A