Project: proton transfer in mixed dimers and trimers of HF and H_2O

This project deals with the interactions of HF **1** with H_2O **2** within their dimers $(HF)_2$ **3** and $(H_2O)_2$ **4**, the mixed dimer H_2O–HF **5** and the mixed trimers $H_2O(HF)_2$ **7** and $(H_2O)_2HF$ **9**, as well as the degenerate multiple proton transfer in the mixed dimer (**5** to **5'**) via the transition structures $(H_3O)F$ **6** and in the mixed trimers (**7** to **7'**) and (**9** to **9'**) via the transition structures $(H_3O)(F_2H)$ **8** and $(H_5O_2)F$ **10**, respectively.
The calculations will be performed using the density functional assigned to you, as follows (detailed instructions below):

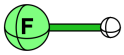
1. compute the structures with Gaussian 16 using the **Def2SVP** basis set and refine using the **Def2TZVP** basis set. Include **Pop=NBORead** and the $NBO keyword line in the refinement calculation to obtain the gas phase NPA charges. Use a checkpoint file for each system.
2. perform counterpoise calculations for the minima after refinement, using the Def2TZVP basis set.
3. recompute the structures (use the checkpoint files) using **SCRF=PCM** (water is the default solvent). Include **Pop=NBORead** to obtain the NPA charges in the implicit solvent.
4. calculate high-level energies (single points) with Orca at the **DLPNO-CCSD(T) aug-cc-pVTZ** level using the gas-phase structures computed in step 1 with the Def2TZVP basis set.

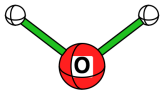
In the first optimization (with the Def2SVP basis set), use **Opt Freq=NoRaman** for the minima and **Opt=(TS,CalcFC) Freq=NoRaman** for the transition structures. In the refinement step (with the Def2TZVP basis set), use **Opt=ReadFC Freq=NoRaman** and **Opt=(TS,ReadFC) Freq=NoRaman**, respectively, and include the keywords **Guess=Read Geom=Check**. You can use Molecule to generate the inputs for the refinement step or copy the input files and use an editor like nedit; in the latter case, make sure that no coordinates are present in the input and be careful to position the $NBO keyword line correctly.
A starting structure for a TS can easily be constructed from the corresponding minimum by moving the hydrogen atoms to obtain a symmetrical (C_s or C_2) structure; no interpolation is required.
The structures for **3**, **4**, **7** and **9** may change significantly when re-optimizing (larger basis set or inclusion of implicit solvent). This may cause the optimization to stop (check the output), due to a linear arrangement of atoms. Should this happen, then restart the calculation using **Opt=Cartesian** (without ReadFC) which is slower but less sensitive to this problem.

Write a concise report:

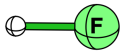
- Introduction, methods, results, discussion, conclusions, as usual.
- Include tables of total energies (a.u.) and relative energies (kcal/mol or kJ/mol).
- Evaluate the interaction energies within the dimers and trimers **3**, **4**, **5**, **7** and **9** at each level.
- How serious is BSSE for these systems?
- Compute the activation energies for proton transfer at each level.
- How does the implicit solvent model affect the structures, the charge distribution and the interaction and activation energies?
- Provide pictures of the computed structures. Pro-tip: use "constrain proportions" when scaling.
- Include relevant distances in the pictures (in Molecule: double-click a bond or add a "line" bond)
- Give literature references where appropriate.

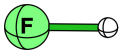
Structures:

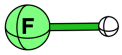
1 HF 

2 H_2O 

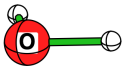
3 $(HF)_2$ structures with Def2SVP and Def2TZVP basis set

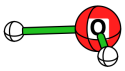
parallel structure 

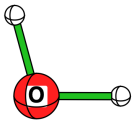


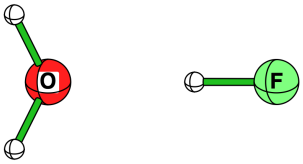
"hydrogen bonded" 

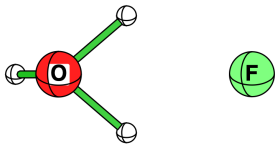
4 $(H_2O)_2$ structure with Def2SVP and Def2TZVP basis set

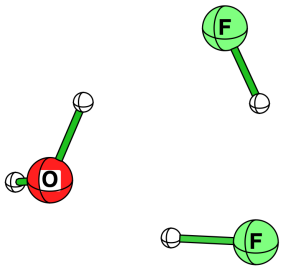
parallel structure 

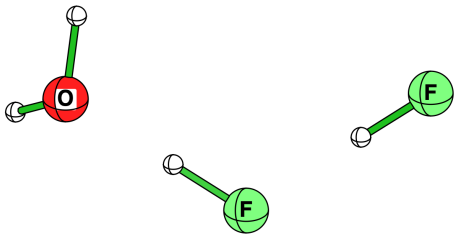


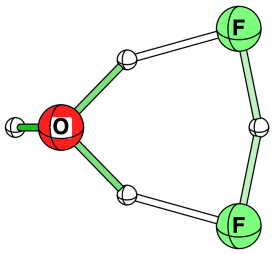
"hydrogen bonded" 

5 H_2O–HF 

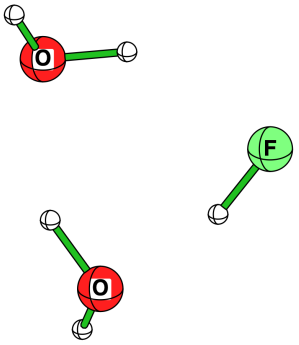
6 $(H_3O)F$ 

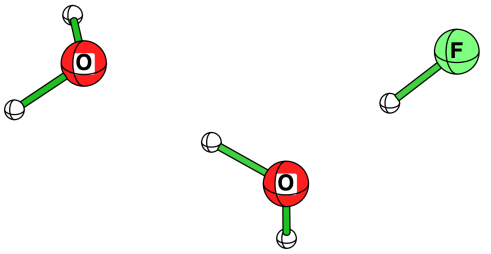


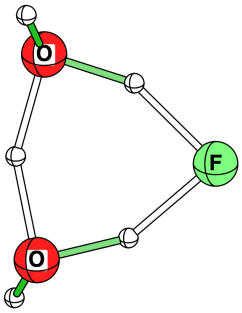




7 $H_2O(HF)_2$ gas phase structure implicit solvent structure **8** transition structure $(H_3O)(F_2H)$







9 $(H_2O)_2HF$ gas phase structure implicit solvent structure **10** transition structure $(H_5O_2)F$