SUPPLEMENTARY INFORMATION

Basis set effects in the description of the Cl-O bond in ClO and XClO/ClOX isomers (X=H, O, Cl) using DFT and CCSD(T) methods

Kenneth Irving[1], Martina Kieninger[1], Oscar N. Ventura[1]*

Fig. S1 shows an overview of the results obtained for different methods, basis sets and reactions. The upper panels show the behavior of different methods with respect to the reactions. It is immediately obvious that the results obtained from the isodesmic reaction (3) are mostly independent of the basis set and the method, giving the more consistent results. If the TAE would be used instead, the PW91 method gives very bad values, but no one would use it anyway. Taking the diatomic molecules as reference, instead of the atoms, reaction (4), give reasonable results (except for TPSS which, again, is a bad choice) but with more dispersion in the limit and smaller than those obtained from reaction (3). Finally, the results obtained from reaction 5 and reaction 6 (not shown) do exhibit larger errors and dispersion of the limit results.

The lower panels show the convergence with the basis sets of the results obtained with some of the methods for the five reactions. The general behavior of the depicted DFT results is similar to that of the CCSD(T) calculations. However, the dispersion of the values obtained from each reaction using the smaller basis sets is larger for CCSD(T) than for the DFT methods. At the large basis set limit however, the DFT methods, especially M06, converge toward a very similar value than CCSD(T) especially if the average of reactions (3), (4) and the TAE are considered. Using a not so large cc-pV5Z basis set, the average results for M06, M06-2X, B2PLYP and CCSD(T) are -18.0, -18.7, -17.3 and -18.3 kcal/mol.

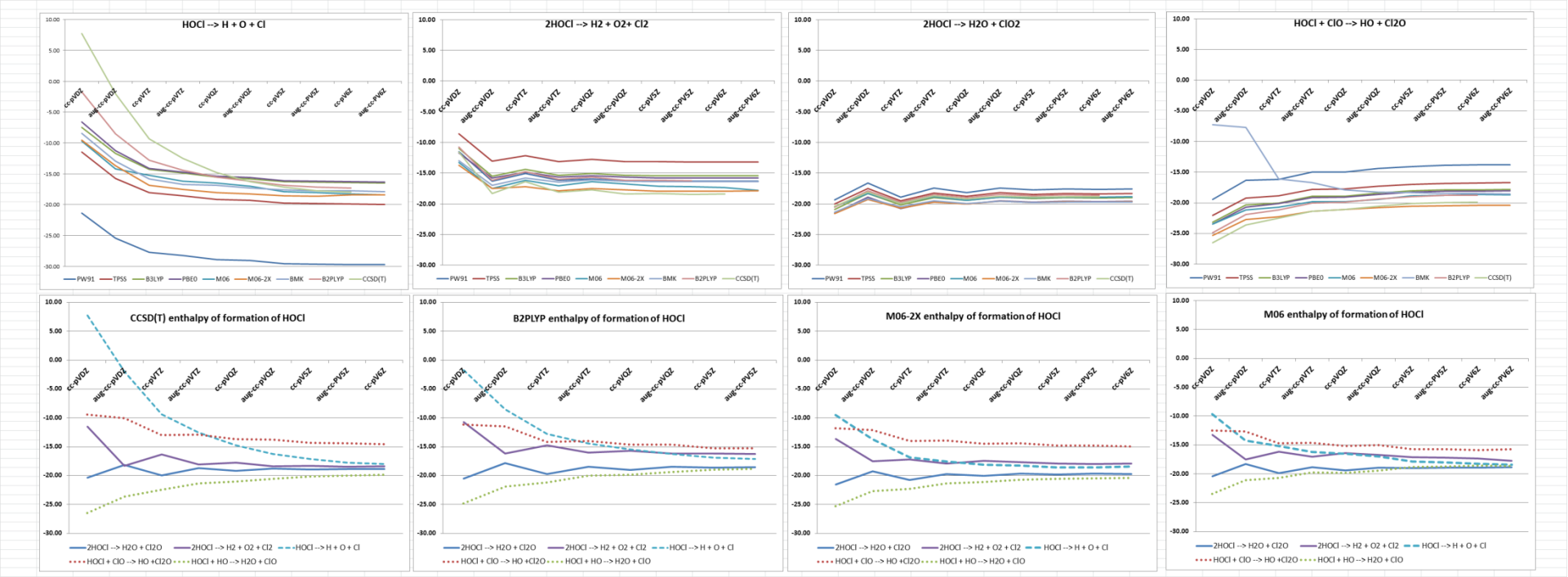

Figure S1. Comparison of the enthalpies of formation of HOCl derived from different reactions with several methods and basis sets (upper panels) and for each method with several basis sets from several reactions (lower panels). All enthalpies of formation are in kcal/mol. See the text for further discussion.

It is clear that no DFT method can provide the same accuracy as CCSD(T) when employing a very large basis set. Of all the methods listed, M06-2X is the one that gives more similar results, in agreement with what we discussed previously. In the same line of thought as before, a combination of the M06-2X method with a not so large basis set (cc-pVQZ) give similar or better results than a CCSD(T) calculation with the same basis set. This can be appreciated, in the case of Cl_2O in the error distribution presented in the panels of Fig. S2.

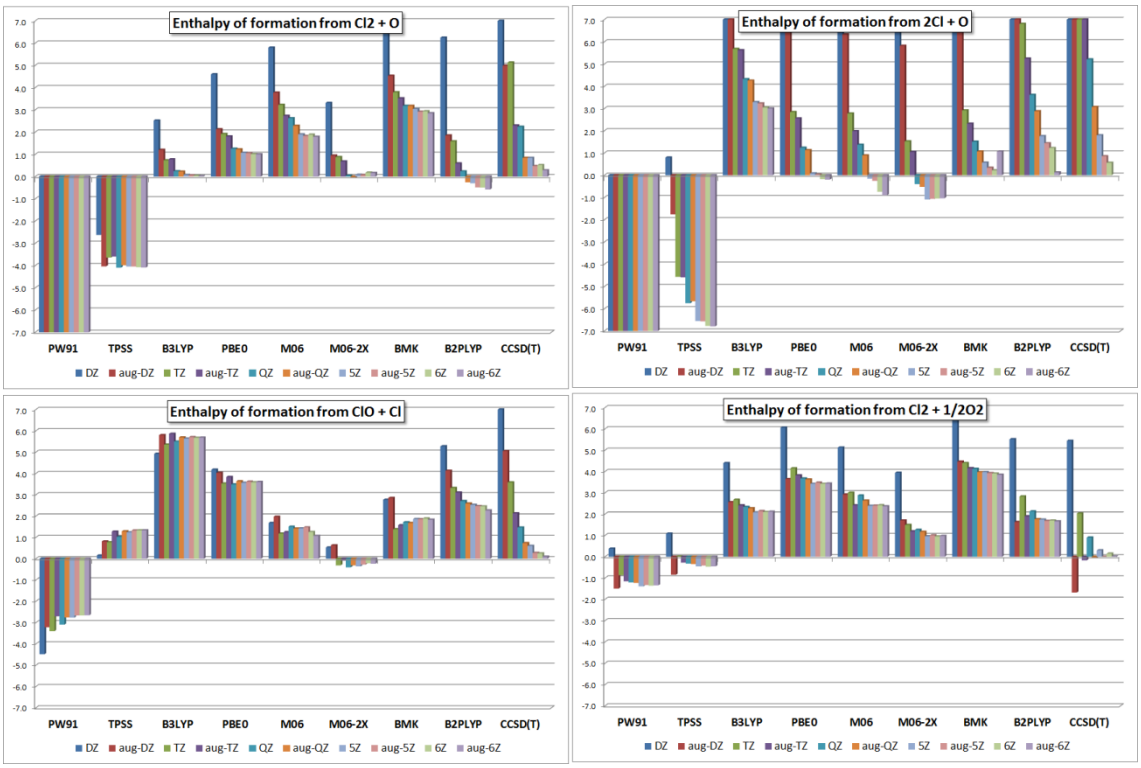

Figure S2. Signed error on the calculated enthalpies of formation of Cl_2O (in kcal/mol) derived from different reactions using different methods and basis sets