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Supplement of

Base synergy in freshly nucleated particles

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S1 Refined Single Point Energies

Engsvang and Elm (2022) benchmarked the ammonia addition and sulfuric acid evaporation energies from the large $(SA)_{10}(AM)_{10}$ FNP. They found that ωB97X-D3BJ/6-311++G(3df,3pd) single-point energies correlated well and gave low error compared to the DLPNO-CCSD(T_0)/aug-cc-pVTZ (Riplinger and Neese, 2013; Riplinger et al., 2013) reference values. We have extended this benchmark to investigate the larger basis sets (def2-TZVPD, ma-def2-TZVP and ma-def2-QZVPP) with the ωB97X-D3BJ functional using a subset of the DLPNO reference values calculated by Engsvang and Elm (2022). This dataset contains 216 $(SA)_9(AM)_{10}$ cluster configurations, 279 $(SA)_{10}(AM)_{10}$ and 87 conformers of $(SA)_{10}(AM)_{11}$. Figure S1 presents the error in the binding energy of several methods, calculated relative to DLPNO-CCSD(T_0)/aug-cc-pVTZ.

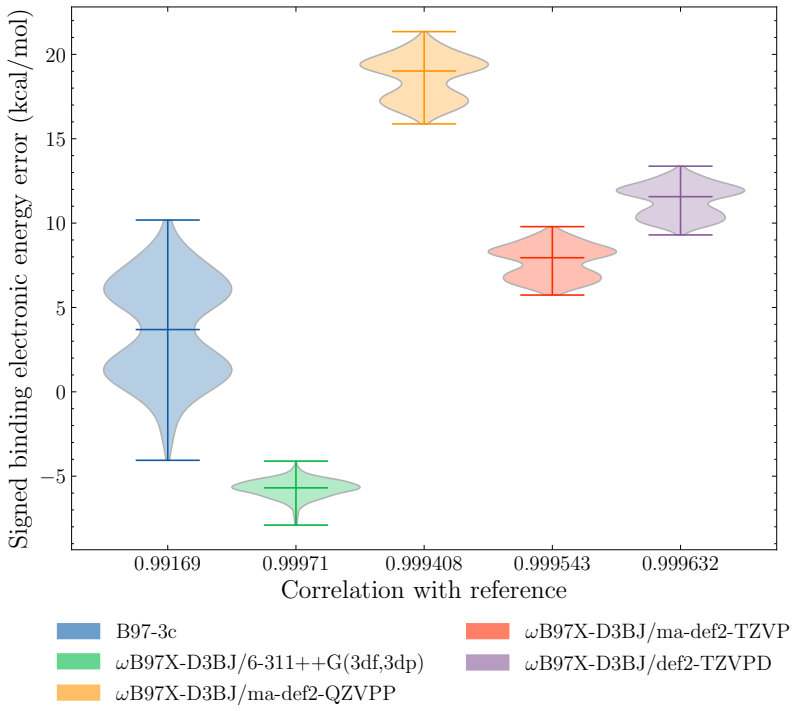


Figure S1. Electronic binding energy errors of the $(SA)_9(AM)_{10}$, $(SA)_{10}(AM)_{10}$, and $(SA)_{10}(AM)_{11}$ clusters compared to the DLPNO-CCSD(T_0)/aug-cc-pVTZ reference values. The x-ticks show the person correlation value.

In general, there is an improvement, in the form of a lower spread, when applying a higher level single-point energy compared to only using B97-3c. The Def2 basis sets generally lead to too positive binding energies and show a double distribution. The double distribution is also present for B97-3c which is consistent with using a basis set based on the Def2-type basis. The upper distribution are the $(SA)_{10}(AM)_{10}$ clusters and the lower distribution originates from the $(SA)_9(AM)_{10}$ and $(SA)_{10}(AM)_{11}$ clusters. This is likely due to the clusters with an equal number of base-acid pairs being more favorable yielding a numerical larger free energy and thus a larger relative error.

We furthermore tried the augmented Jensen basis set (pc) (Jensen, 2001, 2002) and augmented correlation consistent (cc) basis set (Dunning, 1989) but the SCF procedure failed to converge for most of the configurations due to linear dependencies in the basis. The few that did converge showed similar large errors to the Def2 basis sets. The emergence of linear dependencies is linked to the addition of many augmented diffuse functions and not the pc or cc basis set themselves.

The large 6-311++G(3df,3pd) Pople basis set shows the lowest binding energy error with a narrow distribution around -5.7 kcal/mol. This is probably due to a fortuitous cancellation of error. We speculate that the error does not show a double distribution because the relative errors are not large enough. Figure S2 presents the errors in addition energies. The addition

energies are calculated by the addition of an SA molecule to the $(SA)_9(AM)_{10}$ cluster, yielding $(SA)_{10}(AM)_{10}$, and the addition of an AM molecule to the $(SA)_{10}(AM)_{10}$ cluster, yielding $(SA)_{10}(AM)_{11}$. Reference values are calculated at the DLPNO-CCSD(T_0)/aug-cc-pVTZ level of theory. "Lowest" refers to the error using the lowest energy conformers at the given level of theory and "DLPNO conformers" uses the conformers lowest at the DLPNO level of theory.

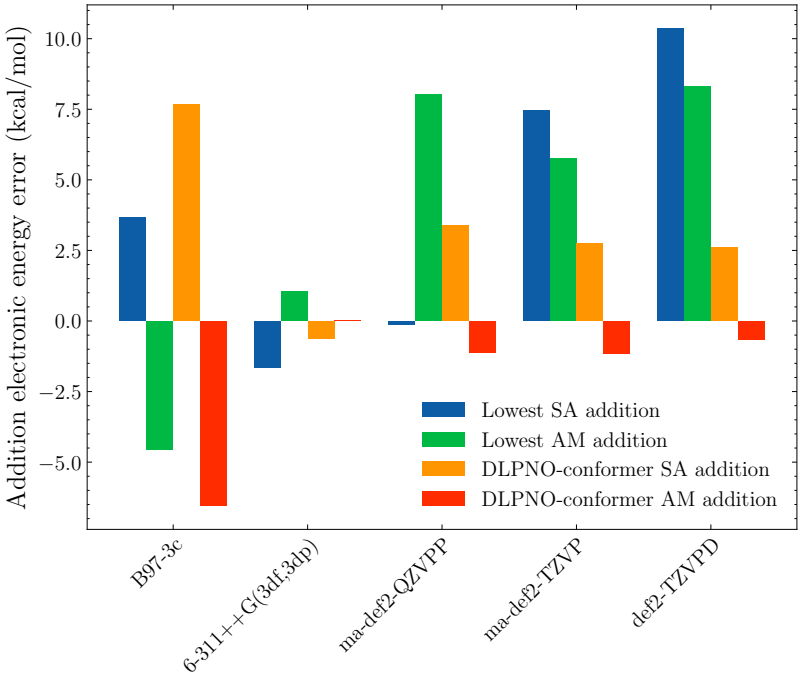
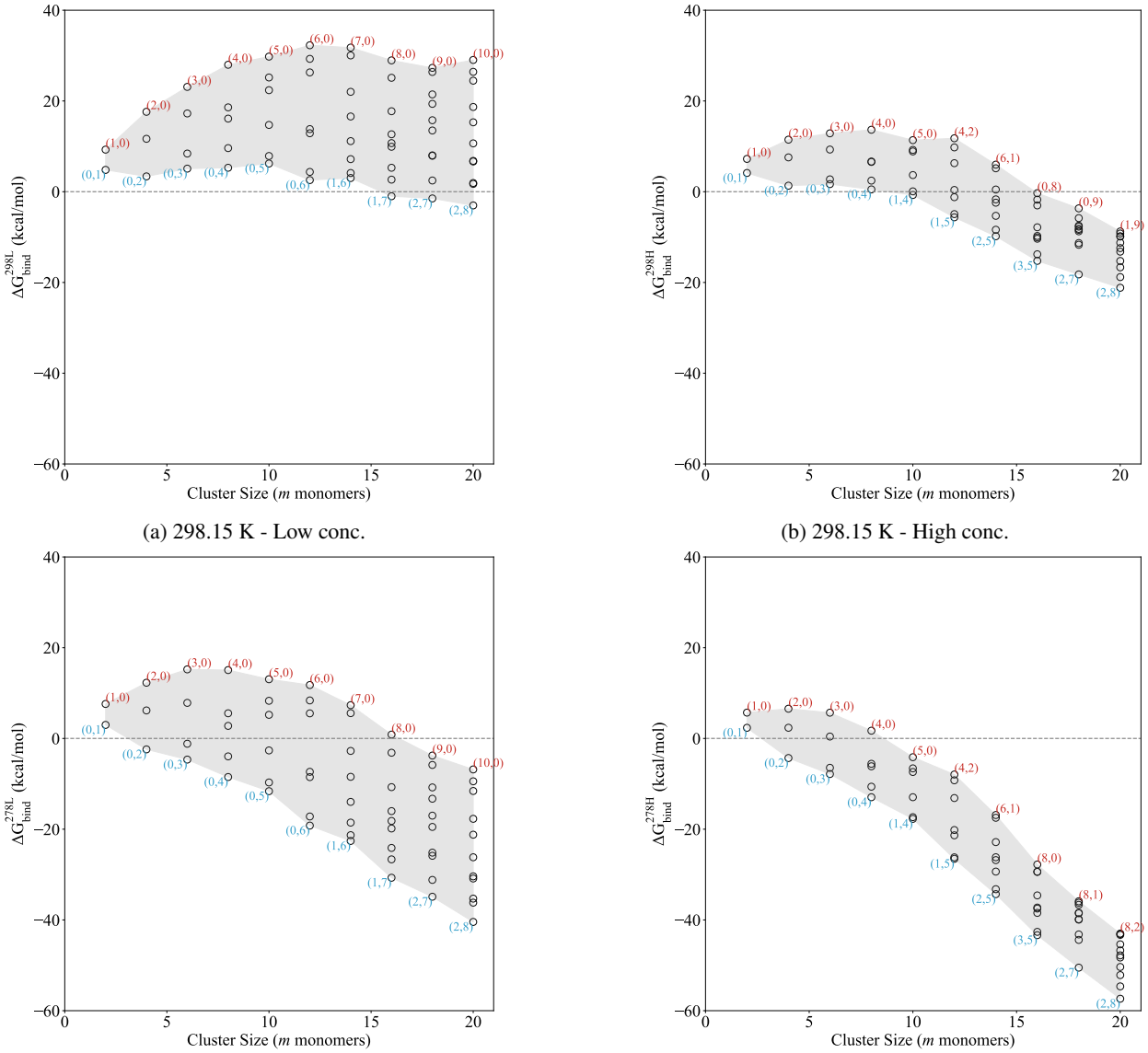


Figure S2. Addition electronic energy errors of the addition of SA from $(SA)_9(AM)_{10}$ to $(SA)_{10}(AM)_{10}$, and AM addition from $(SA)_{10}(AM)_{10}$ to $(SA)_{10}(AM)_{11}$ DLPNO-CCSD(T_0)/aug-cc-pVTZ reference values. "Lowest" is the error using the lowest energy conformers at the given level of theory and "DLPNO conformers" is a comparison between the conformers lowest at the DLPNO level of theory.

Similar to above we see quite large errors for B97-3c, and the ωB97X-D3BJ functional using the def2-TZVPD, ma-def2-TZVP and ma-def2-QZVPP basis sets. Again, we observe the ωB97X-D3BJ functional with the 6-311++G(3df,3pd) to have the lowest errors in all cases. While this is likely a fortuitous cancellation of errors, it appears to be systematic for the systems studied. Based on the previous study by Engsvang and Elm (2022) and the findings here, we will employ the ωB97X-D3BJ/6-311++G(3df,3pd) for refining the single point energy of the clusters in the current work. However, we emphasize that it would be worth to test other approaches for obtaining higher level single point energy corrections in the future.

S2 Free energies at given conditions for [SA] = 10^6 molecules cm^{-3}



(a) 298.15 K - Low conc.

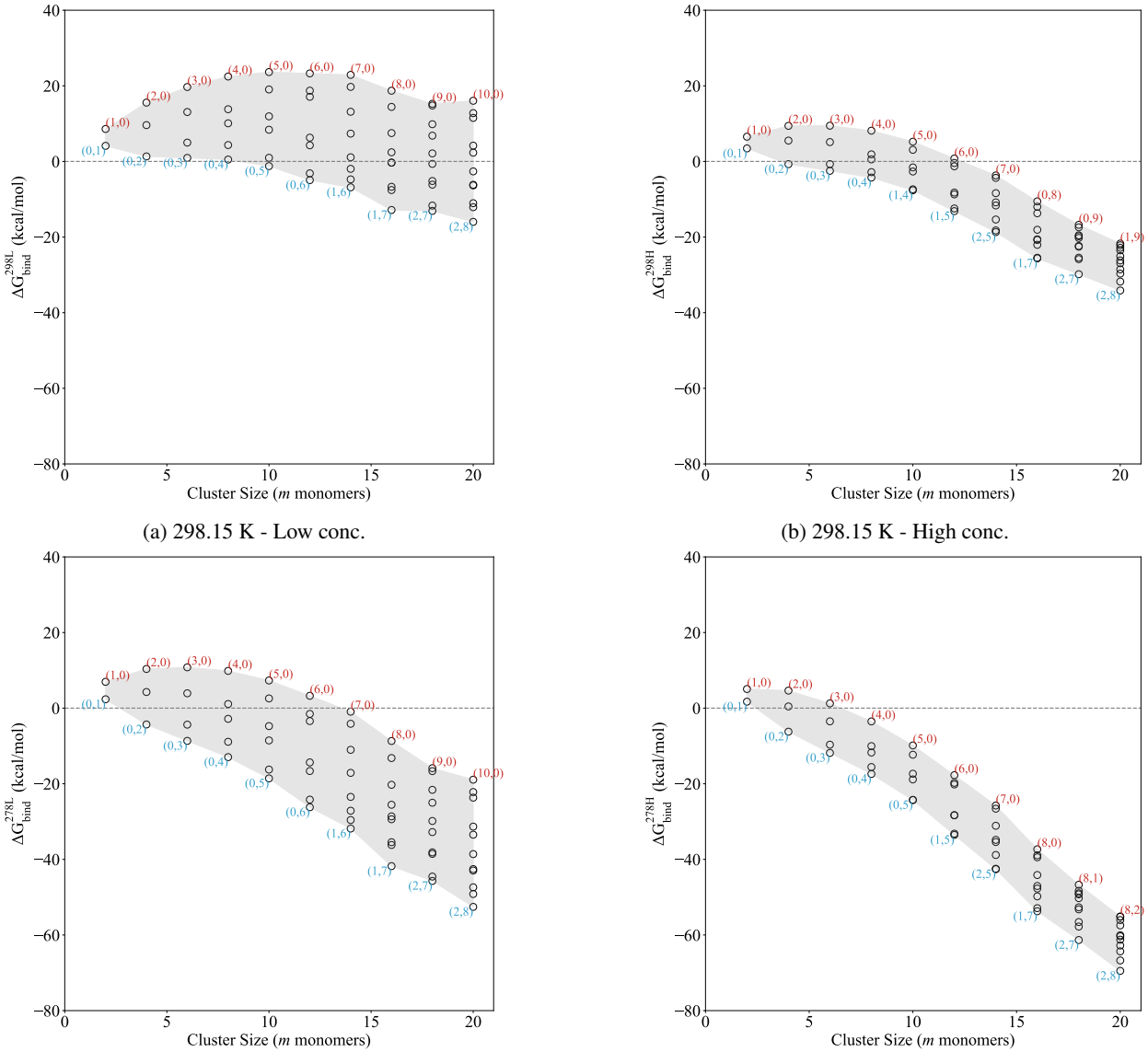
(b) 298.15 K - High conc.

(c) 278.15 K - Low conc.

(d) 278.15 K - High conc.

Figure S3. Binding Gibbs free energy, at the ωB97X-D3BJ/6-311++G(3df,3pd)//B97-3c level of theory of the $(SA)_n(AM)_x(DMA)_{n-x}$ clusters, with $n = x$ between 1 and 10, at given condition of temperature (298.15 K and 278.15 K) and different monomer concentration. Monomer concentrations of [SA] was fixed at 10^6 molecules cm^{-3}. "High conc." refers to [AM] = 10 ppb, [MA] = [DMA] = 10 ppt. "Low conc." refers to [AM] = 10 ppt, [MA] = [DMA] = 1 ppt.

S3 Free energies at given conditions for [SA] = 10^7 molecules cm^{-3}



(a) 298.15 K - Low conc.

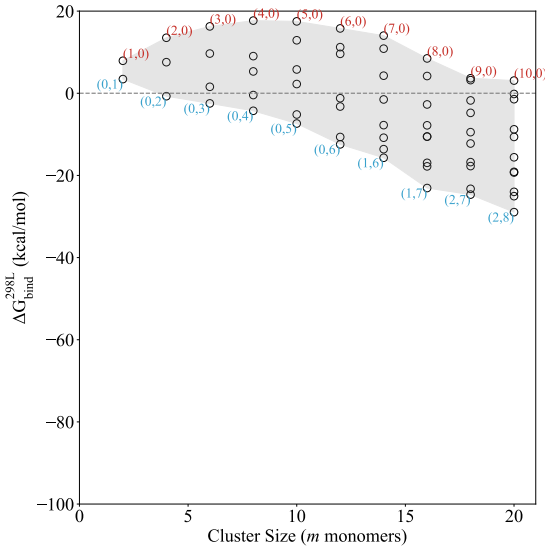
(b) 298.15 K - High conc.

(c) 278.15 K - Low conc.

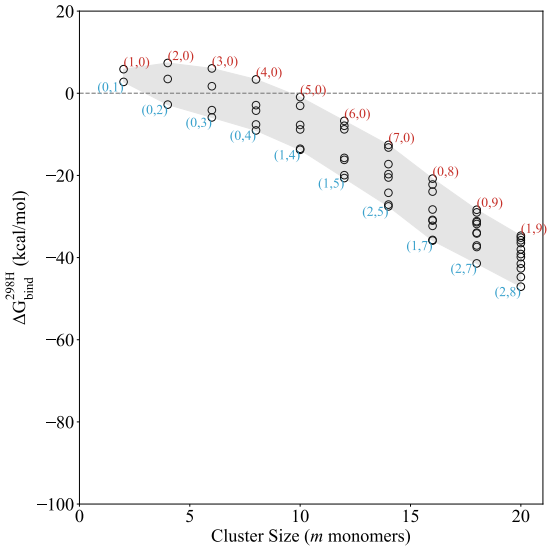
(d) 278.15 K - High conc.

Figure S4. Binding Gibbs free energy, at the ωB97X-D3BJ/6-311++G(3df,3pd)//B97-3c level of theory of the $(SA)_n(AM)_x(DMA)_{n-x}$ clusters, with $n = x$ between 1 and 10, at given condition of temperature (298.15 K and 278.15 K) and different monomer concentration. Monomer concentrations of [SA] was fixed at 10^7 molecules cm^{-3}. "High conc." refers to [AM] = 10 ppb, [MA] = [DMA] = 10 ppt. "Low conc." refers to [AM] = 10 ppt, [MA] = [DMA] = 1 ppt.

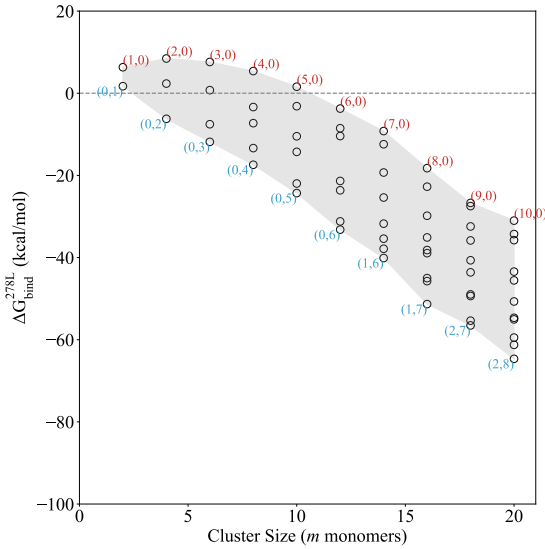
S4 Free energies at given conditions for [SA] = 10^8 molecules cm^{-3}



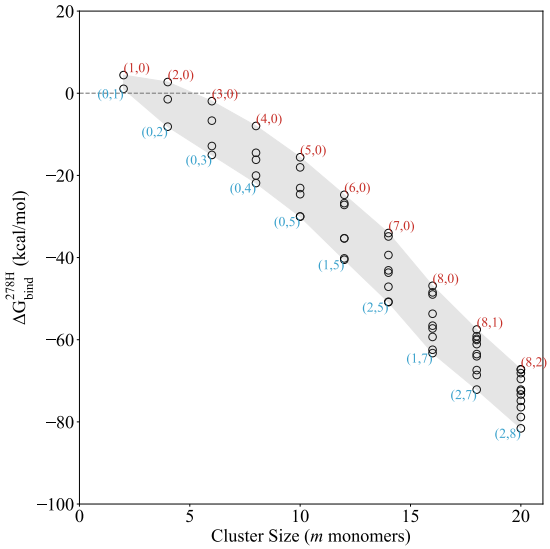
(a) 298.15 K - Low conc.



(b) 298.15 K - High conc.



(c) 278.15 K - Low conc.



(d) 278.15 K - High conc.

Figure S5. Binding Gibbs free energy, at the ωB97X-D3BJ/6-311++G(3df,3pd)//B97-3c level of theory of the $(SA)_n(AM)_x(DMA)_{n-x}$ clusters, with $n = x$ between 1 and 10, at given condition of temperature (298.15 K and 278.15 K) and different monomer concentration. Monomer concentrations of [SA] was fixed at 10^8 molecules cm^{-3}. "High conc." refers to [AM] = 10 ppb, [MA] = [DMA] = 10 ppt. "Low conc." refers to [AM] = 10 ppt, [MA] = [DMA] = 1 ppt.

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