Responses to the Comments of the Reviewer

General comment

RC: *The manuscript by Zhang et al. is devoted to the role that organic acids (OA) may play in new particle formation from methanesulfonic acid (MAS) and methylamine (MA)molecules. It is based on high-level quantum chemical calculations of the formation free energies of selected MA-MSA-OA ternary clusters and on results obtained from ACDC (Atmospheric Cluster Dynamics Code) simulations. The main conclusion of the paper is that the formic acid (ForA) molecule is of particular interest because ForA might have an important role in MSA-driven new particle formation (NPF) in relevant atmospheric conditions. The various factors that affect the enhancing potential of the organic acids, especially ForA, on MSA-MA NPF were also thoroughly analysed.*

The work is technically well performed and the results of the calculations well support the conclusions. The manuscript is almost clearly written and should be interesting for the community of atmospheric chemists.

I recommend publication of this manuscript after the following (minor) points have been taken into account.

AC: Thanks for the positive comments. We have revised the manuscript to further enhance its quality.

Special Suggestions and Comments

RC: 1) *When comparing the various dicarboxylic acid molecules considered in the calculations, it is found that only maleic and glutaric acid can interact via their two carboxylic groups. It is however suprising that such configuration has not been found for Succinic acid. This has to be discussed.*

AC: Thanks for the suggestion. We agree with the reviewer that we should discuss why other dicarboxylic acids interact with $(MA)_1(MSA)_1$ only via one -COOH group. In the revised manuscript, the following sentences have been added:

"For OxaA, the configuration involving the interaction of two -COOH groups with $(MA)_1(MSA)_1$ was not located. This results from the fact that the two -COOH groups in OxaA are directly linked and thereby OxaA cannot adapt a conformation where both -COOH groups interact with other molecules in the clusters. For MalA, SucA and AdiA, the binding free energies for the configuration with interactions of both -COOH groups with $(MA)_1(MSA)_1$ are higher than that for the configuration with the interaction of single -COOH group with $(MA)_1(MSA)_1$. This could result from the high deformation energy penalty when these three OAs interact with $(MA)_1(MSA)_1$ via two -COOH groups. An interesting phenomenon was that MaleA and SucA have different interaction pattern although they have the same number of C-atom. Such difference mainly results from the existence of double bond linker between the two -COOH groups of MaleA. The double bond linker allows MaleA to interact with $(MA)_1(MSA)_1$ via two -COOH groups and slight deformation as shown in Fig. S1."

We added the Figure S1 in the revised Supplement.

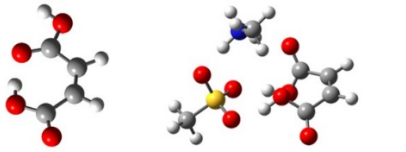

Figure S1. Lowest Gibbs free energy conformations of MaleA and $(MSA)_1(MA)_1(MaleA)_1$ cluster at the ωB97X-D/6-31++G(d,p) level of theory. The red balls represent oxygen atoms, blue ones for nitrogen atoms, gray ones for carbon atoms, and white ones for hydrogen atoms.

RC: 2) *Although the ACDC code has been presented elsewhere, it is quite disappointing not having here a brief presentation of its main inputs and outputs. In particular, this would greatly improve understanding of section 3.4 and Figure 6.*

AC: Thanks for the comment. We agree that a brief presentation of basic formula and main inputs and outputs of ACDC should be provided. In the revised manuscript, the following sentences have been added to present basic formula and main inputs and outputs of ACDC:

"Briefly, the core of ACDC is to employ the birth-death equation (Eq. (2)) to describe the time-dependent cluster distributions:

$$\frac{dc_i}{dt} = \frac{1}{2}\sum_{j<i}\beta_{j,(i-j)}c_j c_{(i-j)} + \sum_j \gamma_{(i+j)\to i}c_{i+j} - \sum_j \beta_{i,j}c_i c_j - \frac{1}{2}\sum_{j<i}\gamma_{i\to j}c_i + Q_i - S_i \quad (2)$$

where subscripts (*i, j, i-j, j-i* and *i+j*) represent different clusters or monomers in the system, c_i represents the number concentration of *i*, $\beta_{i,j}$ denotes the collision rate coefficient between *i* and *j*, $\gamma_{(i+j)\to i}$ denotes the evaporation rate of a cluster *i+j* into smaller clusters (or monomer) *i* and *j*. Q_i represents an additional outside source term of *i* and S_i represents other sink terms for *i*. The collision rate coefficients were calculated by hard sphere kinetic gas theory as:

$$\beta_{i,j} = \left(\frac{3}{4\pi}\right)^{\frac{1}{6}}\left(\frac{6k_bT}{m_i} + \frac{6k_bT}{m_j}\right)^{\frac{1}{2}}\left(V_i^{\frac{1}{3}} + V_j^{\frac{1}{3}}\right)^2 \quad (3)$$

where k_b is the Boltzmann constant, *T* is the temperature, and m_i and V_i are the mass and volume of *i*, respectively. The evaporation rates were calculated using detailed balance as:

$$\gamma_{(i+j)\to i} = \beta_{i,j}c_{\mathrm{ref}}\exp\left\{\frac{\Delta G_{i+j} - \Delta G_i - \Delta G_j}{k_bT}\right\} \quad (4)$$

where ΔG is the formation free energy of the cluster, c_{ref} is the reference monomer concentration at 1 atm, which is the pressure at which ΔG was calculated (Mcgrath et al., 2012)."

"We used the calculated thermodynamic data of $(MSA)_x(MA)_y(OA)_z$ ($0 \le y \le x+z \le 3$) clusters as input for ACDC simulations to obtain the cluster formation pathways and new particle formation rates."

RC: 3) *Finally, when comparing the DeltaG values, it should be clearly stated that the discussion in the paper is based on the absolute values, whereas relative values are given in Tables and Figures. Then, « higher values » in the text correspond in fact to « lower values » in the Tables/Figures.*

AC: We are actually already discussing the relative values in the text. For instance, at Line 145 we write: "Generally, the ΔG values of the $(MSA)_1(MA)_1(OA)_1$ clusters vary from -12.69 to -17.87 kcal mol^{-1}, and are 2.49-7.67 kcal mol^{-1} higher than that of the $(MSA)_2(MA)_1$ cluster." In this context higher refers to less negative, which is also the case if you look at Figure 2a (compare the gray bar of MSA with the brown bars of the OAs). However, we agree with the reviewer that this should be clearer in the text as it is always convoluted to discuss negative quantities. We have modified the first occurrence where we discuss the free energies (i.e. the above sentence) to reflect this issue. In the revised manuscript, the original sentence "Generally, the ΔG values of the $(MSA)_1(MA)_1(OA)_1$ clusters vary from -12.69 to -17.87 kcal mol^{-1}, and are 2.49-7.67 kcal mol^{-1} higher than that of the $(MSA)_2(MA)_1$ cluster." was revised as

"Generally, the ΔG values of the $(MSA)_1(MA)_1(OA)_1$ clusters vary from -12.69 to -17.87 kcal mol^{-1}, and are 2.49-7.67 kcal mol^{-1} higher (i.e. less negative) than that of the $(MSA)_2(MA)_1$ cluster."