

Interactive comment on “From quantum chemical formation free energies to evaporation rates” by I. K. Ortega et al.

Anonymous Referee #1

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The paper by Ortega et al. presents the results of a computational study on stability of molecular clusters composed of sulfuric acid, ammonia, and amines. The criterion used for stability is the evaporation rate, which is calculated from detailed balance using the association rate constant and equilibrium constant of the cluster formation. The association rate constant is evaluated from the collision rate theory approximation. The equilibrium constant is calculated using the Gibbs free energy of cluster formation obtained from quantum chemical calculations at several levels of theory.

The major conclusion of this study is that for clusters containing base molecules, fission is an important decay pathway in addition to that by evaporation of single monomer molecules. Thus, because of the existence of very stable clusters of specific composition, a system that would have overcome the critical size in terms of monomer

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evaporation can still slide back to pre-critical size by fission to two smaller clusters.

The subject of this study is an issue of significant interest to the atmospheric science community, as recent experimental and theoretical evidence indicates that amines and sulfuric acid may play a central role in the nucleation and growth of atmospheric nanoparticles. From my viewpoint, the manuscript has two significant qualities that make it worthy of publication. First, the authors have conducted a systematic characterization of different quantum chemical methods and selected the one providing the most accurate results. Second, this study has highlighted the importance of local minima on the nucleation potential energy surface, showing that the decay pathway typically neglected by the classical nucleation theory could be very important in atmospheric new particle formation and that the widely used application of the nucleation theorem to atmospheric observations of nucleation may produce erroneous results regarding the composition and size of critical clusters.

The paper should certainly be published. However, there is an important caveat that needs to be addressed beforehand. Namely, the authors should explicitly state that the conclusions made in this study are based on an approximate treatment of association rate by collision theory. This simplified approach may greatly overestimate the association rate for clusters, leading to non-uniform (i.e., size- and structure-specific) variations in the rate constant. Lower association rates would result in lower dissociation rates with non-uniform scaling between different clusters.

From a chemist's prospective, one may allude to the performance of collision theory versus [variational] transition state theory ([C]VTST). In CVTST, the dissociation rate is calculated explicitly whereas the association rate is obtained from detailed balance, i.e., the approach exactly reverse to the one used here. I realize that the use of CVTST for cluster evaporation rates, such as it is done in the dynamical nucleation theory, is computationally unfeasible at the present for large multicomponent clusters. Thus, I propose to add a paragraph with an explicit discussion of the limitations of the utilized approach and how those limitations may affect the results and the conclusions made

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in this study.

A couple of minor technical comments:

1. Is there a point of including the data obtained by CBS-4M in the paper? This method, using uncorrelated HF for geometry and frequency calculations, is clearly inadequate for the task of cluster calculations.
2. It is not clear what does 'high level combination' refers to in line 24 on page 27336

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