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Atmospheric Chemistry and Physics Discussions

Interactive comment on "A Monte Carlo approach for determining cluster evaporation rates from concentration measurements" *by* Oona Kupiainen-Määttä

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The manuscript presents a series of MCMC simulations aimed at determining cluster evaporation rates from concentration measurements. The topic of the paper is interesting and important . The paper's well-written and easy to follow. After a thorough validation, the proposed approach could possibly be developed into a useful theoretical tool linking cluster concentrations and evaporation rates. However, I have to recommend major revisions because the number of issues to be addressed before the paper can be further considered for publication is quite large and some of them are serious..

Comments

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Discussion paper

I. Introduction is a way too self-referential, dedicated almost exclusively to own work and fails to acknowledge important contributions made by others. It also contains some misleading statements that need correction. 1.1 The clusters considered in the paper are relevant directly to the Ion -Mediated Nucleation (IMN), which is an important source of new particles in the Earth's atmosphere (see e.g. Geophys. Res. Lett., 27, 883-886, 2000; J. Geophy. Res., 106, 4797-4814, 2001; Atmos. Chem. Phys., 8, 2537-2554, 2008; Atmos. Chem. Phys., 12, 11451-11463, 2012). A brief discussion on these matters accompanied by the corresponding references should be included in the Introduction to the revised manuscript. 1.2. The discussion on quantum-chemical studies on charged sulfuric acid-ammonia and sulfuric acid-ammonia-water clusters is limited to Almeida et al., 2013; Olenius et al., 2013b and fails to acknowledge a number of relevant contributions made by others (e.g. JPC A 116(24) 5886-5899, 2011; J. Phys. Chem., A, 117, 133-152, 2013; Atmos. Chem. Phys., 9, 4031-4038, 2009; PCCP, 10, 7073 - 7078, 2008). References to the aforementioned and other relevant studies should be included in the revised manuscript. 1.3. MC has been widely used in nucleation and cluster formation research since 2000s. In particular, a well-known MC-based DNT (Dynamic Nucleation Theory) has been developed by Kathmann and Garrett with co-workers at the PNNL (e. g. PRL82(17):3484-3487, 1999. JPC B 105(47):11719-11728, 2001, J.Chem. Phys. 120(19):9133-914, 2004; . It would be useful to include a brief discussion on earlier applications of MC to nucleation and cluster formation in the revised manuscript. 1.4. The statement that "At the same time, modeling of particle formation has also advanced greatly in the past few years. For the first time theoretical predictions of cluster distributions (Olenius et al., 2013b) and particle formation rates (Almeida et al., 2013) agree qualitatively with experimental findings." is partly misleading because predictions of particle formation rates in Almeida et al., 2013 clearly disagree with the experimental data (Chem. Phys. Lett„ 624, 111-118, 2015). The statement should be corrected. 1.5. The author states that "This approach has been shown to give qualitative agreement with experiments (Almeida et al., 2013; Olenius et al., 2013b), but several very drastic assumptions are

involved. First-principles molecular dynamics simulations (Loukonen et al., 2014a, b) have shown that one harmonically oscillating cluster structure is far from a realistic description of the thermal motion of molecules in a cluster, implying that the traditional way of computing cluster formation free energies may be a rough approximation". However, this statement is obviously misleading because conclusions obtained using lower level theory such as ab initio MD Loukonen et al., 2014a, b are not applicable to results obtained using higher level theory such as ab initio or DFT. Unharmonic corrections for DFT level with typical scaling factors of 0.95-0.99 are very low and cannot significantly impact cluster formation rates. Also , the impacts of local minima on resulting thermochemical properties can be easily calculated using the Gibbs-Boltzmann distribution. This statement should be either modified or deleted. II. The source of thermochemical data used for computing evaporation rates in Table 1 is unclear. The MC fitting data were compared to Ortega et al. (2014) only. The author states that "Also evaporation rates estimated from quantum chemical Gibbs free energies Ortega et al. (2014) are presented in Table 1 for comparison". However, I wasn't able to find any data on Gibbs free energies in Ortega et al. (2014). Neither delta H nor delta S values were found in there. Delta G values seem to be missing in Ortega et al. (2014), too. Please, clarify the source of the data and include computations of evaporation rates based on quantum data obtained by others in Table 1 of your paper. III. Temperature dependency of evaporation rates is very important; however, the analysis of the temperature-dependent evaporation rates is missing. I would suggest the author to perform a study of evaporation rates for a few clusters at the room temperature and T=273.15 K and compare MC fitted evaporation rates with those obtained using quantum methods in Ortega et al. (2014) and other related studies. IV. It is well-known that uncertainties in measured cluster concentrations may be pretty big due to impurities, charging and other issues. The influence of the experimental uncertainties on MC fitted evaporation rates and fragmentation in the mass spectrometer should be discussed in some detail.

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