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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Formation of binary ion clusters from polar vapours: Effect of the dipole-charge interaction" *by* A. B. Nadykto and F. Yu

Anonymous Referee #1

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Summary: The paper extends the existing classical Kelvin-Thomson theory for ion induced aerosol nucleation (IIN) by including the interaction of the charge (core ion) with the dipole moments of the surrounding condensable vapour molecules. Binary ion induced nucleation is considered in general and the case of sulphuric acid and water is studied which is of importance for atmospheric aerosol nucleation. The size and composition of the critical cluster is calculated for several combinations of temperature (273 and 283 K), relative humidity (85 and 95%) and gas phase concentration of sulphuric acid (10ˆ7, 10ˆ8 and 10ˆ9 cm-3). Applying their extended theory the authors find that the number of molecules in the critical cluster is considerably reduced compared to both classical neutral binary homogeneous nucleation as well as ion-induced nucleation as calculated from the Thomson equation.

General comments: Recently, ion-induced nucleation in the atmosphere has received considerable attention. Currently it is not possible to consistently explain observed atmospheric aerosol nucleation events with classical aerosol nucleation models, be it through ternary nucleation, binary nucleation or ion-induced nucleation. The presented extension of theory makes the effort to take into account an additional effect which has not been considered by IIN models before but it does not overcome the general difficulty of classical aerosol nucleation models: Because bulk properties of solutions are used in these models (e.g. surface tension, density and dielectric constants) their applicability to atmospheric nucleation events, where the critical cluster is composed of $<<$ 1000 molecules might be generally limited. This should at least be discussed and a caveat about this fact should be added.

A thorough comparison of the results with Delta G curves (and especially the maximum of the Delta G curve marking the critical cluster) resulting from molecular thermodynamic data of ion clusters is suggested. It would strengthen the extended theory considerably if the results were comparable. For example, the thermodynamic data is available for H3O+(H2O)n clusters as well as for the HSO4-(H2SO4)m. This point is similar to the suggestion of reviewer 2.

It is quite surprising that the effect of the extension of theory (charge-dipole-interaction between ion and gas phase dipoles) is by far larger than the Thomson effect. This should be discussed and a physical explanation should be presented. The Thomson term describes the interaction of the charge with the close-by condensed molecules through interaction of the charge with a dielectric. The condensed molecules are much closer to the charge than the gas phase molecules and the net effect of the binding forces from the charge is expected to be larger on the condensed molecules than on the gas phase molecules because the interaction force is strongly dependent on distance.

It should be noted that the extended theory is not able to explain preferences in IIN depending on the sign of the ion charge (c.f. Kusaka et al., JCP 1995). Such sign

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preferences exist.

The validity of the theory strongly depends on equation 9, an equation which is supposed to be derived in a publication by Nadykto et al., which is not published yet. In Nadykto et al. (made available to the reviewers) the equation is not derived rigorously but reference is given to another publication by Korshunov which is difficult to obtain. Therefore it would be helpful if Korshunov's concepts of the charge-dipole-interaction would be reviewed briefly in the current manuscript and reference to Korshunov would be given.

The paper would benefit if nucleation rates were derived additionally.

Overall, the paper makes a useful extension to classical ion induced nucleation theory but it needs revision in order to address the points outlined above before it can be published in ACP.

Specific/Technical comments:

* Figure 1 is missing (printed Fig. is same as Fig. 5)!

* Figure 2: axis are mislabelled!

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 4927, 2003.