Atmos. Chem. Phys. Discuss., 11, C5256–C5258, 2011
www.atmos-chem-phys-discuss.net/11/C5256/2011/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Ab initio studies of $O^{\vec{-}}_{bf2}(H_2O)_{\vec{n}}$ and $O^{\vec{-}}_{3}(H_2O)_{\vec{n}}$ anionic molecular clusters, $n\vec{\leq}12$" *by* N. Bork et al.

N. Bork et al.

nbor@space.dtu.dk

Received and published: 22 June 2011

We thank the reviewer for the positive review of our manuscript.

We agree that the pressure and temperature dependence of the distributions of cluster sizes are highly interesting in order to assess the atmospheric implications of these findings. This is performed in a new section which is inserted in this reply (the mentioned Fig. 1 is new and has been appended as well). This section will be inserted in the resubmitted version of the manuscript.

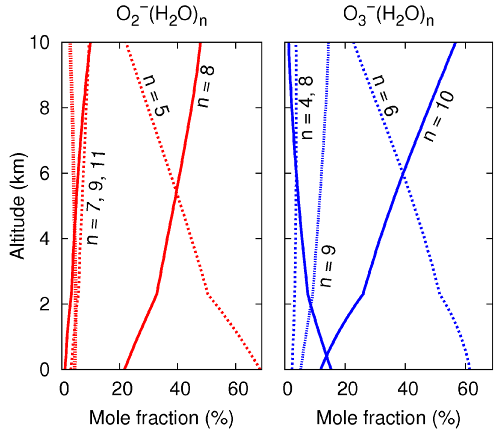
Hereby, the implications of the results are more readily accessible e.g. for inclusion in a larger model of the troposphere, and consequently the manuscript should become of interest for a broader audience.

3.4 **Tropospheric size distributions** It is well known that for several gas phase reactions, the degree of hydration may be important both for the kinetic and thermodynamic properties (Kurtén et al., 2007; Bandy and Ianni, 1998). Hence, it is of interest to study the distribution of the clusters at varying temperatures and pressures corresponding to typical tropospheric conditions (Mhin et al., 1993). Therefore, we have determined the mole fractions at varying altitudes, assuming a constant lapse rate of 6.5 °C, a ground level temperature of 15 °C and a constant relative humidity (RH) of 25%. Further, thermal equilibrium is assumed and both sources and sinks are neglected. Thereby, the mole fractions of the various clusters readily can be deduced via Eq. 2. The results are shown in Fig. 8. For clarity, only the 5 most probable clusters are shown.

First, we note that the mole fractions are very sensitive to the amount of water vapor. In more humid atmospheres, the clusters readily grow while smaller clusters are more probable at drier conditions. However, under all conditions will clusters of multiple sizes co-exsist. Also apparent from Fig. 8, is that smaller clusters dominate at lower altitudes due to the higher temperatures favoring water evaporation. However, only under extremely dry conditions (RH $<$ 0.1%) are the distributions dominated by clusters smaller than n = 5.

Secondly, the distribution around the altitude of freezing is interesting, here found at ca. 2.3 km, whereafter gaseous H_2O must equilibrate with ice rather than liquid water. This effect delays the tendency of cluster growth at increasing altitudes due to decreasing temperatures, and is seen as a kink in Fig. 8.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 13947, 2011.



Mole fraction as function of altitude. The distributions are very sensitive to the water vapor pressure - here shown for 25% RH. For clarity only the 5 most populated structures are shown. At the altitude of freezing, ca. 2.3 km, the water vapor equilibrate with ice in stead of liquid water- hence the kinks.

Fig. 1.