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Interactive comment on “Accommodation coefficient of HOBr on deliquescent sodium bromide aerosol particles” *by* M. Wachsmuth et al.

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Response to the note on purely solubility driven uptake: In the setting of the experiment used to obtain the present results, gas-phase reactants and products are separated from the particles in a denuder. The characteristic time for the release of soluble gases from the particles (microseconds for these very small particles below 100nm in diameter, limited by liquid phase diffusion) is much shorter than that of their separation in the denuder (20ms, limited by gas-phase diffusion). Therefore, soluble gases are completely removed from the aerosol. This means that reaction in the liquid phase must be faster than re-evaporation from the particles, if the uptake should be limited by mass accommodation. We will emphasise this more explicitly in the revised manuscript.

1. Response to the doubts on the identity of HOBr: The bromine isotopes are generated from short-lived precursor Se isotopes deposited on a quartz surface. Decay of a Se isotope means that a highly energetic (20 MeV) electron is ejected from the

nucleus resulting in a highly ionised Br atom and a high density of ions and radicals in the immediate vicinity of the surrounding gas. The formation of a stable volatile brominated compound of course critically depends on the composition of the carrier gas. The only way radiochemists can assess the chemical speciation of short-lived nuclides in the gas-phase is by observing their sorption behaviour and reactivity with surfaces of different materials and comparing it with their expected macroscopic counterpart. In the present case, a gas-chromatography type experiment (see Eichler et al., 2000, for another case) directly revealed that only one species had been formed, and that it exhibits an adsorption enthalpy on polar surfaces that indicates its ability to undergo H-bonds (Wachsmuth et al. 2002). Furthermore, its only very weak interaction with CBr4 indicated independently that the molecule is relatively polar. When O2 was removed from the carrier gas, no gas-phase brominated molecule was observed. We do not believe that Br radical could escape our set-up at atmospheric pressure. To test for BrO we added NO2 at up to 10ppm to observe any changes in the behaviour described before through formation of BrONO2, which was not the case. So, it seems likely that the local radical chemistry is strong enough to convert an intermediate (radical, possibly excited) into HOBr. We have also shown that the system can be driven to produce labelled Br2 by adding molecular Br2 in excess (Wachsmuth et al. 2000) or HBr by adding an excess of H2 (Wachsmuth et al. 2002). We will extend the section describing the generation of the HOBr molecules to make it more clear, although the details are given in the cited references.

2. Response to the question whether the accommodation coefficient could be unity: The error given (30 percent) was a very conservative estimate driven by the surface estimate from the measurement of particle diameters using the differential mobility analyser (DMA) coupled to the CPC. Whereas the diameter can be very precisely measured (to within about 2 percent), a few larger particles beyond the range observed by the DMA as well as a counting efficiency eventually lower than unity of the CPC could lead to an underestimation of the total aerosol surface to volume ratio. It seems that the probability is larger that the aerosol surface is larger than estimated from the

measurements, which would make the accommodation coefficient derived from the measurements more probable to be smaller than the fitted value. However, there is a further systematic unknown in this system: we did not assess the mixing time between the two gases. If the characteristic time for mixing is on the same order of magnitude or even 10 percent of the characteristic time for reaction, then the observed uptake would have to be corrected for this and this would push the accommodation coefficient to higher values. We will add this "mixing" caveat to the revised version.

Interactive comment on Atmos. Chem. Phys. Discuss., 2, 1, 2002.

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