Response to Bill Simpson:

The authors thank Prof. Simpson for his insightful comments.

On page 14172, line 16, the concept of depletion of snow bromide is mentioned. Is it possible to give some quantification to the mass balance of bromide at the surface based upon these experiments? Specifically, it seems like the calibration of the CIMS means that total liberated bromine atoms per time liberated from the snow are measured. Integration of these produced bromine atoms over time should then indicate mass loss of bromide from the snow. How does this mass loss compare to the initial mass of bromide in the snow? I would presume that the liberated bromine is much less than bromine frozen into the snow, which would then mean that some bromide is not available on the surface and/or diffusion of non-surface bromide to the surface is a limiter of bromide available for reaction. This calculation may by very crude, but it might give interesting insight into the nature of bromide on the surface and/or limitations on bringing bromide to the surface.

The bromide content in the artificial snow samples was quite low (in an absolute sense, as well as in a relative sense compared to chloride). For a typical 'BASE CASE' snow sample (40 g of snow, 0.5 M NaCl, prepared with reagent grade NaCl), the available Br^{-} is calculated to be no more than ~9 × 10^{17} ions (assuming the stated impurity of < 0.01% by weight places an upper limit on the Br^{-}). The area under the Br_2 and BrCl curves was calculated for a BASE CASE run (i.e. shown in Figure 3a) from t = -40 min to t = +20 min (i.e. starting at the point O_3 was turned on, somewhat arbitrarily ending at a point that Br_2 levels had decreased significantly). Scaling the areas with the flow rate (210 sccm) gives the yields or Br_2 and BrCl in molecules. The total consumed Br^{-} from these yields was calculated to be ~ 1 × 10^{17} ions (2 Br^{-} per Br_2 and 1 Br^{-} per BrCl). This represents at leasta 10th of the available Br^{-}. Thus, a large fraction of the available Br^{-} is indeed consumed during the reaction. At t = 20, the [BrCl] are still quite high (so there is clearly Br^{-} remaining that is available). It is consistent with known (aqueous) chemistry that a decrease in Br^{-} favours BrCl production over Br_2 production. This is largely due to the fact that as $[Br^{-}]$ decreases, the equilibria that govern Br_2 and BrCl in solution are affected. Particularly:

$BrCl + Br^{-} \leftrightarrow Br_2Cl^{-}$

$Br_2 + Cl^{-} \leftrightarrow Br_2Cl^{-}$

For example, Fickert et al. (Activation of Br_2 and BrCl via uptake of HOBr onto aqueous salt solutions, *JGR*, **104**, D19, 1999), show that the yield of BrCl is greater than the yield of Br_2 as the relative amount of Br^{-} vs. Cl^{-} decreases: BrCl is the dominant product in the reaction of HOBr(g) with aqueous halide solutions (with [NaCl] = 1 M and [NaBr] < 10^{-5} M). It would be difficult to determine to what extent the results we see are due to some limitation of bringing bromide to the surface, in addition to the simple fact of its being depleted in the brine.

Furthermore, it is not possible for us to determine how much of the snow sample was accessed by the air flow, so obtaining closure at long times (even if all available Br^{-} is located at the snow surface) is not necessarily to be expected. This also makes it difficult to assess whether or not there is bromide that is not available for reaction (i.e. if there is a limitation on bringing bromide to the surface).

A sentence has been added to Section 3.1 to state that "over the course of a typical 'Base Case' experiment, we estimate that 10 – 15% of the total bromide content may react."

On page 14176, section 3.6, there is a discussion of the necessity for acid pH, and relatively low pH appears important. That is a very important result of this work with important atmospheric implications. Do the authors have an idea of the mechanistic reason for necessity of such acid pH? The pKa of HOBr is about 8.7, and that of HOCl is reported as about 7.5. Both of these pKa values would indicate that all of these acid pH values (including the value of 5.9, where dihalogen production was not observed), both hypohalous acids should be highly protonated. The trend in lower pKa for HOCl than HOBr appears to be in agreement with the observations of reduced production of chlorine at pH 4.3 while bromine is still produced. However all of the pre-freezing pH values are quite low compared to these pKa values. Can the authors speculate mechanistically about why these pH values are required?

One possibility for the strong pH dependence observed for Cl_2 production is protonation of HOCl being a rate-limiting step. Donaldson et al. ("Detailed Study of $HOCl + HCl \rightarrow Cl_2 + H_2O$ in Sulfuric Acid", *J. Phys. Chem. A*, **101**, 1997) suggest that the reactive uptake of HOCl onto sulfuric acid solutions doped with HCl proceeds with the rate-limiting first step being protonation:

$HOCl + H^+ \leftrightarrow H_2OCl^+$
$H_2OCl^+ + Cl^- \rightarrow Cl_2 + H_2O$

According to equilibrium thermodynamic models, the brine chloride concentrations should be a function of temperature. Our observation of no temperature dependence for the Cl_2 yields for temperatures above the eutectic suggests that Cl_2 production is independent of brine $[Cl^-]$, consistent with HOCl protonation as the rate-limiting step in Cl_2 production.

Section 3.6 and 3.8 have been re-worded to suggest this possibility.

Response to specific comments:

p14168, line 15. I presume that the temperatures reported later are those of the reaction chamber (5K warmer than the chiller), but please clarify this point.

Yes. This was clarified in the text (in Materials and Methods Section 2.1)

p14168, line 25. What is the pressure at the region of the SF6- ion source? Does the electron attachment occur at near atmospheric pressure, or at close to the IMR pressure (2.5 Torr)?

The SF_6^- ion source is at the IMR pressure of 2.5 Torr. Full description of the apparatus can be found in Thornberry and Abbatt (Phys. Chem. Chem. Phys, **6**, 2004) as mentioned in the text.

p14169, line 6. A bias of -14V is mentioned here, and also another bias is mentioned earlier. What potentials are these compared to (are they compared to the chamber wall or the mass spectrometer or what)?

The potentials are referenced to the overall ground, which is the chamber wall. Full details given in Thornberry and Abbatt (2004).

p14169, line 24. How was the Cl2 final mixing ratio measured? Same question for the Br2 mixing ratio in the standard?

The final mixing ratio was determined from the initial X_2 pressure and its successive dilution in N_2 (determined from pressure, and calculated assuming ideal gas behaviour). A sentence was added to clarify this point (in Material and Methods Section 2.3).

p14170, line 14. I think this should say counts per second for the ion source.

This was added.

*p14170, line 25. I think that the resistivity of pure water is 18 M-ohm * cm. The "cm" is missing.*

Thank you. This has been fixed.

p14171, line 1. Please relate the impurity level in these NaCl samples to that of sea water.

A sentence has been added in Section 2.4 to address this.

p14171, line 21. I think the unit of chamber volume should be centimeters cubed (squared is listed).

Thank you. This has been fixed.

p14172, line 1. Was bromide analyzed for in these samples or not? Please mention.

Bromide was not analyzed because its signal was obscured by chloride's large signal. A sentence has been added to clarify this.

p14175, line 14. This wording is a little confusing. A reduction in the photolysis rate is listed as Cl2»BrCl. That could be read that Cl2 is much faster than BrCl or much more reduced. Please reword to be clearer.

This has been fixed.