

## ***Interactive comment on “Uptake coefficient of H<sub>2</sub>O<sub>2</sub> on ice” by H. Yan and L. T. Chu***

### **Anonymous Referee #2**

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Comments on the manuscript entitled: “Uptake coefficient of H<sub>2</sub>O<sub>2</sub> on ice” Author(s): H. Yan and L.T. Chu MS No.: acp-2011-865

#### General comments:

This paper reports the results of uptake kinetic experiments of hydrogen peroxide on ice. Experiments were performed in a double-jacketed cylindrical flow reactor at a temperature range 190–220 K and H<sub>2</sub>O<sub>2</sub> partial pressure ranging from  $7.9 \times 10^{-6}$  to  $4.7 \times 10^{-5}$  Torr. The authors observed a non-reversible uptake of H<sub>2</sub>O<sub>2</sub> to ice and they used first order kinetics to calculate the initial uptake coefficient. From a physical chemistry perspective, the results are interesting; however the authors are working with such high H<sub>2</sub>O<sub>2</sub> concentrations that make these studies not interesting from an atmospheric chemistry perspective. The authors also used TPD to get insights about the interactions of H<sub>2</sub>O<sub>2</sub> with the ice surface, but again with using such a high

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H<sub>2</sub>O<sub>2</sub> concentration (the minimum exposure 6600 Langmuir compared to 1 Langmuir= 1 monolayer) it will be very hard to get information about ice-H<sub>2</sub>O<sub>2</sub> interactions since you need to start with coverage that is less than a monolayer. Moreover, as H<sub>2</sub>O<sub>2</sub> is desorbing from the surface, water from the ice substrate is desorbing as well which can affect the interpretation of the results. The authors mentioned this, but did not make an effort to explain how this affects their interpretation of the results in terms of H<sub>2</sub>O<sub>2</sub>-ice interactions. With such high concentrations, it is not surprising at all to get aggregation and multilayer formation on the surface and it is also not surprising to observe a zero-order desorption in thick multilayers. The authors relied on the common leading edge of their TPD chromatograms to get kinetic information, but one puzzling thing is that, for the uptake studies, the authors showed in Figure 2, that the adsorption of H<sub>2</sub>O<sub>2</sub> on ice is dependent on the partial pressure of H<sub>2</sub>O<sub>2</sub> however, in zero-order TPD the desorption does not depend on the coverage meaning the amount of H<sub>2</sub>O<sub>2</sub> adsorbed. I think that the authors should elaborate on this more and explain why they think this is happening. There are key issues to be addressed in the manuscript. After the authors revise the manuscript and address the reviewers' questions, I will leave it to the editor to decide if this manuscript is suitable for publication in ACP or not.

#### Specific comments:

1- The introduction showed repetitive sentences in which the authors tried hard to give an atmospheric relevance of their work but I think they did not succeed. For instance, P30092-P30093, the authors mentioned the importance of H<sub>2</sub>O<sub>2</sub> photolysis in ice on tropospheric chemistry, however, the concentrations and temperature used in this study are not relevant to lower troposphere. 2- P30093, L16-21, the authors summarized the results of earlier uptake studies, however in the discussion section they did not make an effort to compare their results to these studies and did not discuss why they are different. 3- P30095, L4 the authors stated that their flow reactor was at a pressure of 0.270 Torr. However, they did not explain if under this low pressure they observe evaporation of their ice film and if they observed any, how did they correct for this. 4-

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P30097, L11-15, the authors reported initial uptake coefficients of H<sub>2</sub>O<sub>2</sub> on ice, but later on P 30102, they stated that the uptake coefficient on fresh ice (not exposed to H<sub>2</sub>O<sub>2</sub>) and aged ice (exposed two-four times to H<sub>2</sub>O<sub>2</sub>) showed same uptake coefficient. So if both experiments showed the same result how is this termed initial uptake? Also since TPD results in Fig.6 showed formation of multilayers shouldn't their uptake experiments show this as well? Otherwise it seems that TPD and uptake experiments are contradicting each other. 5- P30100-30101, based on Fig.2 the authors suggested that their surface is porous, however by looking at Fig.2 it seems that, the initial uptake and within experimental was almost constant as a function of increasing ice-film thickness. Only the first two points showed a change and if we consider the error bars, they are constant within experimental error. If there are more detailed studies on the initial part it will be more convincing since there are only two points on the initial part. 6- Page 30103, the authors used a zero order kinetic because all of the chromatograms have a leading edge, however, and due to the broadness of the peak, it seems more than one peak resides there, did the authors do any fitting for their chromatograms, it seems that there is multilayer formation and not aggregate formation. Hydrogen bonding will be very strong so it is not surprising to have lateral interactions. Looking at figure 2, I think it is just more complicated than a zero order kinetic. Also it is not surprising that, they see a change in T<sub>d</sub> with increasing the film thickness since more H<sub>2</sub>O from the ice will desorb along with H<sub>2</sub>O<sub>2</sub>. I would recommend that the author show us a TPD profile for H<sub>2</sub>O in the absence of H<sub>2</sub>O<sub>2</sub>. Additionally I think the authors should explain better what does the shifts in T<sub>d</sub> mean instead of just stating there was a shift 7- Page 30124, the authors labeled panel b in fig. 6 wrong. I think it should be water desorption otherwise there caption does not describe the figure properly and the text on page 30103 does not agree with the figure.

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Interactive comment on Atmos. Chem. Phys. Discuss., 11, 30091, 2011.

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