

Interactive comment on “Uptake coefficient of H₂O₂ on ice” by H. Yan and L. T. Chu

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We thank the anonymous reviewer for his/her thoughtful comments and criticism. Our responses to the major points are below.

General comments:

Agree with both reviewers. The H₂O₂ pressure is higher than the atmospheric H₂O₂ concentration. Since we have determined that the initial uptake coefficient is a function of pressure and temperature, the data can be extrapolated to the atmospheric conditions with a good confidence level. The typical [H₂O₂] in the polar atmosphere is ~1-2 ppbv, and our experimental [H₂O₂] is ≥10 ppbv. We have modified the manuscript to state that the results can be extrapolated to the atmospheric conditions on the basis of γ_t as a function of $P_{H_2O_2}$ and temperature. The figures were replotted to reflect the extrapolation.

The conditions for TPD experiments are very different from that in Fig. 3. The des-
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orption profile contains the information of the lateral H₂O₂ interaction and interaction between H₂O₂ and ice. If there is no lateral interaction, H₂O₂ will probably not form multilayers on ice at ~200K and 1×10^{-5} Torr. Water desorbs at ~225-230K, after H₂O₂ desorbs from the surface. At high H₂O₂ exposure (amount in the gas phase), the lateral interaction among adsorbed H₂O₂ is dominant. The complicated TDP profile is separated by desorption temperatures, T_d . For example, for the first desorption peak, T_d increases as surface coverage increases, which is an indication of the zero-order desorption kinetics. The main purpose of the TPD profile is to show that there is a lateral interaction at ~200K so that the including proposed aggregation pathway is supported. This statement is now added in Section 3.5. At high exposure or multilayer coverage, H₂O₂ is heated off "layer-by-layer" from the top of the multilayer and [H₂O₂(ad)] can be treated unchanged, so that desorption is zero-order kinetics. Fig. 3 shows the H₂O₂ loss on ice, and there is higher probability for H₂O₂(p) to be aggregated together at high $P_{H_2O_2}$. At very high $P_{H_2O_2}$, γ is expected to be independent of $P_{H_2O_2}$ because of H₂O₂ condensation on ice. We revised the manuscript and expanded the discussion.

Specific comments:

H₂O₂ concentration. γ was determined as a function of pressure and temperature, and results can be extrapolated to atmospheric conditions (~1-2 ppbv (Bales et al. 1995)). We revised the Introduction section, and removed repetitive sentences and added that results can be extrapolated to atmospheric conditions.

P30093, the comparison of our results with a published stick coefficient (Conklin et al.) was presented in the discussion section. Both Clegg and Abbatt (2001), and Pouvesle et al. (2010) have studied the uptake amount (isotherms). A direct comparison between the initial uptake coefficient and uptake amount cannot be made. We now added an H₂O₂ uptake amount datum at 220 K, and the result is in agreement with Clegg and Abbatt. The uptake amount is lower than that of Pouvesle et al., and a brief discussion is included in the revised manuscript.

P30095. Since the vapor pressure at 190 K is $\sim 3 \times 10^{-4}$ Torr, the evaporation rate is relatively low. We stated that the effect of the ice-film's volatile nature on the film

thickness is negligible because of the short experimental time scale to measure γ_w (P30095, L23-25). Also, we deposited additional amount ice toward end of the reactor to minimize the ice evaporation.

P30097/P30102. The confusion and unclear sentences were revised. We added a sentence: effect of the surface H_2O_2 contamination on uptake coefficient is studied using experimental H_2O_2 exposure amount on ice, in Section 3.4, and a confusing sentence was revised to: the results show that the measured γ_w value represents the initial H_2O_2 uptake coefficient on the ice surface well, within the experimental uncertainty, and a small reversed rate (R 1) from low H_2O_2 surface coverage does not significantly affect the measured loss rate constants.

Yes, the measured uptake coefficients include multilayer interaction. Kinetic model includes it as an aggregation term since the relative portion of aggregation (multilayer or island) is affected by $P_{\text{H}_2\text{O}_2}$. This is clarified in Section 3.5 in the revised manuscript (see general comment)

P30100/30101. We added the description of ice films to indicate that the prepared ice film was not smooth and then used the model to correct. Vapor-deposited ice films can be porous and have internal surface areas (Keyser and Leu, 1993a,b). The ice film used in this study was opaque from human eye observations. This is due to light scattering from ice granules of the film.

Now, we explained weak thickness dependence in Section 3.1. With $\gamma_t = 1.1 \times 10^{-3}$ ($\eta \approx 0.28$ at $N_L = 13$), the fitted result indicates the H_2O_2 loss rate is fast compared to pore diffusion, only a small fraction of the internal surface (near surface layer) is available for H_2O_2 uptake. Thus, the dependence of γ_w on h is not strong, and γ_w is nearly independent of h at $> 4.0 \mu\text{m}$.

P30103. In TPD experiments, due to high exposure, H_2O_2 is multilayer on ice. In the uptake coefficient measurements, the amount of H_2O_2 lost on ice is approximately 10^{12} molecules/cm² (coverage), and we used the term "aggregation" to describe the lateral interaction. We thought aggregation represented an adsorbed H_2O_2 attracts nearby adsorbed H_2O_2 , but it is not multilayer adsorption. We revised the paper to clarify the

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processes and confusion.

Zero-order desorption kinetics describes the desorption of multilayer H_2O_2 from ice only. Others processes cannot be described by the zero-order kinetics, and the TPD process is very complicated. A H_2O desorption profile was included in the plot; however, it is mixed within the plots. We re-plotted the figure, and now the H_2O (pure ice) desorption profile is visible.

P30124. The label and plots were revised. It is H_2O desorption in Panel b.

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

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