

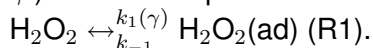
## ***Interactive comment on “Uptake coefficient of H<sub>2</sub>O<sub>2</sub> on ice” by H. Yan and L. T. Chu***

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We thank the anonymous reviewer for his/her thoughtful comments and criticism. Our responses to the major points are below. We have revised the introduction section and stated that the goal of this study is to determine the H<sub>2</sub>O<sub>2</sub> loss rate (uptake coefficient  $\gamma$ ) on ice. The process is described by R1



The initial uptake coefficient,  $\gamma_w \propto 4k_1/\omega$ , was determined when an ice film was freshly prepared and the ice surface was clean. Experimentally, the loss of H<sub>2</sub>O<sub>2</sub> on ice surfaces can be described using first-order kinetics when the ice surface is clean (i.e. reverse rate in R1 is negligible).

In the revised manuscript, we tried to distinguish the initial uptake coefficient, uptake amount (equilibrium surface coverage), and surface coverage (coverage). The term,

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surface coverage, describes the amount of adsorbate on a surface either at the equilibrium (isotherms) or non-equilibrium in literature. The uptake amount,  $[\text{H}_2\text{O}_2(\text{ad})]_{ss}$ , is usually determined under the gas-surface steady-state equilibrium condition, i.e.,  $k_1[\text{H}_2\text{O}_2] - k_{-1}[\text{H}_2\text{O}_2(\text{ad})]_{ss} = 0$ . The uptake amount and the initial uptake coefficient are two different physical parameters and cannot be compared directly. However, we did add an uptake amount datum at 223K in the comparison section. The uptake amount ( $5 \times 10^{12}$  molecules/cm<sup>2</sup> at  $1.1 \times 10^{-5}$  Torr and 222.9 K) is in agreement with the result ( $1 \times 10^{12}$  molecules/cm<sup>2</sup> at 228 K) reported by Clegg and Abbatt (uptake or surface coverage), but it is lower than that reported by Pouvesle et al. ( $1.7 \times 10^{14}$ , equilibrium surface coverage). A comparison and discussion is included in Section 5. Aggregation of adsorbed  $\text{H}_2\text{O}_2$  is a pathway. It is not a dominated pathway and was ignored at warm temperatures.

The justification to study this atmospheric chemistry issue was revised in the introduction section and some partially repetitive sentences were removed.

P30093. The reversible uptake is added to the text. The reversible uptake is used to describe an observed desorption profile (Clegg and Abbatt, Pouvesle et al.).

Uptake coefficient is a function of surface coverage. We assume that the experimental uptake coefficient  $6 \times 10^{-3}$  was estimated using the first-order kinetics expression and two data points from the uptake profile/breakthrough curve (e.g., Hynes et al., JGR 2002, doi:10.1029/2001JD001557). If there are no interactions among adsorbed  $\text{H}_2\text{O}_2$  molecules, the observed uptake coefficient usually decreases as surface coverage increases. The estimated uptake coefficient would be a lower limit. If there are attractive lateral interactions,  $\gamma$  increases as surface coverage increases. At lower temperature, e.g.,  $T=213\text{K}$ ,  $\text{H}_2\text{O}_2$  has tendency to condense on ice, and Pouvesle et al. used the BET isotherm to fit their experimental results. We also observed  $\text{H}_2\text{O}_2$  zero-order desorption kinetics, suggesting attractive interactions among  $\text{H}_2\text{O}_2(\text{ad})$ . Thus, it is difficult to say the estimated value,  $6 \times 10^{-3}$ , is a lower limit for the  $\text{H}_2\text{O}_2/\text{ice}$  system.

P30096. We revised the determination of the vapor pressure of 93%  $\text{H}_2\text{O}_2$ .

P30097.  $\gamma_w$  is time-independent, and the surface is not saturated. The  $\gamma$  value can be affected by  $\text{H}_2\text{O}_2$  adsorbed on the surface. The first measurement,  $\gamma_w$ , in Fig. 5 was conducted on the clean ice surface, and Fig. 5 shows  $\gamma$  values are constant (within experimental errors). We had tried to say that the  $\gamma_w$  value represents the initial uptake coefficient, within the uncertainty of the experiment. This was revised in the manuscript.

P30097/98. The net signal change from 29753 counts/s to 11133 counts/s is not small in terms of measurements. A similar signal change ( $2 \times 10^{11}$  to  $0.7 \times 10^{11}$  molecule/cm<sup>3</sup>) was recorded in Fig. 1 of Pouvesle et al. and Fig. 6 of Clegg and Abbatt (from 0.19 to 0.18 V). We used 6 data points in the plot ( $\ln[\text{H}_2\text{O}_2]$  vs  $t$ ). The limited data points are constrained by experimental conditions and the loss rate. The plot shows the first-order kinetics reasonably well, but not excellent.

We determined the loss of gas-phase  $\text{H}_2\text{O}_2$  on a clean ice surface (i.e.,  $k_1$  of R1, given  $k_{-1}[\text{H}_2\text{O}_2(\text{ad})] \approx 0$  for clean ice surfaces). The ice surface is neither saturated nor in equilibrium with gas-phase  $\text{H}_2\text{O}_2$ . Adsorption isotherms are determined under the gas-surface equilibrium and Pouvesle et al. measured equilibrium surface coverage. The exponential decay is from the change of gas-surface contact time ( $z/v$ ) in eq (1), and  $\text{H}_2\text{O}_2$  was exposed to more fresh ice surfaces as the injector was pulled out.

P30098/99. We revised the sentence to: Vapor-deposited ice films can be porous and have internal surface areas (Huthwelker et al. (2006) reviewed the ice porosity issue). With  $\gamma_w \approx 0.01$  (Fig. 2),  $\text{H}_2\text{O}_2$  samples top layers of the ice granules. The variation of  $\gamma_w$  with thickness is small. Keyser et al. (1993) documented the observed behavior as well. The fitted parameter  $\tau$  is not very sensitive to the shape of the curve. In the manuscript, we clarify that the correction is an approximation. Experimentally, it is difficult to determine the ice surface area in situ while performing the uptake coefficient measurements.  $\gamma_w$  depends on many factors such as  $\text{H}_2\text{O}_2$  concentration, temperature, and ice surface conditions. We assume that the value,  $6 \times 10^{-3}$ , was estimated at 213 K from Fig. 1 of Pouvesle et al., because the experimental conditions were given at 213 K, and the uptake profile/breakthrough curve at 233 K needs to correct before

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one can estimate loss rate constant using the first-order kinetics. Thus, it is difficult to compare our  $\gamma_t$  values to the estimated value directly. Please note that a difference between Fig. 1 and the uptake profile/breakthrough curve (Fig. 1 of Pouvesle et al.) is that the time in Fig. 1 (0–2.5 ms) is the gas-surface contact time and that the time in Fig. 1 of Pouvesle et al. is the  $\text{H}_2\text{O}_2$  exposure time to the surface. The events (0–2.5 ms) in Fig. 1 occurred within the rapid signal drop ( $t=100\text{s}$ ) in Fig. 1 of Pouvesle et al. Desorption is unlikely the cause, because the  $\text{H}_2\text{O}_2$  desorption occurred in both our experiments and the experiments by Pouvesle et al. and the comparison was at the same temperature ( $k_{-1}$  is the same). However, the ice surfaces for both experiments were prepared differently, and the ice-surface dynamic nature can affect the results (this was added).

Usually, the gas-surface reaction (adsorption) is expressed in terms of the reversible reaction (e.g., Mazel 1996). Experimentally, one measures the net loss of  $\text{H}_2\text{O}_2$  in the gas phase, i.e.,  $\text{rate} = k_1[\text{H}_2\text{O}_2] - k_{-1}[\text{H}_2\text{O}_2(\text{ad})]$ . But, we can treat  $[\text{H}_2\text{O}_2(\text{ad})] \approx 0$  when the ice surface is clean. In terms of the experimental design, we chose experimental conditions to meet the first-order kinetics. Fresh ice was prepared in every experiment, and proper flow conditions were chosen to match measured loss rate constants. This approach was used by many groups and is recommended (e.g., Kolb et al., 2010; Crowley et al., 2010). Also, we did the uptake amount measurements and observed the desorption profile at 223K. The desorption is due to absent gas-phase  $\text{H}_2\text{O}_2$  from the surface, and the surface was warmed by the injector when the injector was pushed back to the starting position.

P30102. Pouvesle et al. determined the equilibrium surface coverage (uptake amount) under the gas-surface equilibrium (isotherms). Adsorption of a small amount of  $\text{H}_2\text{O}_2$ . ... – we refer to the amount of  $\text{H}_2\text{O}_2$  loss on the surface. We revised the text and added the amount ( $3.8 \times 10^{12}$  molecules/cm<sup>2</sup>, determined by integrating the amount of  $\text{H}_2\text{O}_2$  on ice over the experimental time), i.e., surface coverage.

P30104, L12. Precursor state is a mobile weakly bound state, and molecules in a physisorption state are often trapped and stick on the surface.

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P30104, L23. The amount of  $\text{H}_2\text{O}_2$  loss on the surface was determined to be  $\approx 3.8 \times 10^{12}$  molecules/cm<sup>2</sup> (see Section 3.4) by integrating the  $\text{H}_2\text{O}_2$  QMS signal over the experimental time. Using the calibrated  $\text{H}_2\text{O}_2$  QMS signal, the QMS counts can be converted to the number density. The amount is at the low end of submonolayer  $\theta < 0.1$ . This is the amount of  $\text{H}_2\text{O}_2$  exposed to the ice surface (surface coverage). It is not in equilibrium with  $P_{\text{H}_2\text{O}_2} \approx 1 \times 10^{-5}$  Torr. Pouvesle et al. reported equilibrium surface coverages at  $P \approx 10^{-5}$  Torr and 213–233 K.

P30105. Both reverse rates (R3 and R4) were ignored (based on clean ice surfaces). The precursor state is in equilibrium with gas-phase  $\text{H}_2\text{O}_2$ , and R3 is the rate determining-step ( $\text{H}_2\text{O}_2(\text{p}) \rightarrow \text{H}_2\text{O}_2(\text{a})$ ). It can be treated as the first-order kinetics.

P30106. It is coverage, and it is  $\approx 3.8 \times 10^{12}$  molecules/cm<sup>2</sup> ( $\theta < 0.1$ ). Pouvesle et al. reported the equilibrium surface coverage.

P30108. We used the same symbol as the original reference. We changed the symbol per the reviewer's suggestion.

P30109. Uptake coefficient may be estimated from the breakthrough curve using the first-order kinetics expression. The  $\gamma$  value depends on many factors, e.g., surface coverage, temperature, lateral interactions, and ice morphology. Without detailed information, it is difficult to make a direct comparison between estimated uptake coefficient and our  $\gamma_t$  values.

P30110. We revised the discussion of  $\text{H}_2\text{O}_2$  lifetime.

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

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