

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

Anonymous Referee #1

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General

The authors have measured uptake kinetics for H₂O₂ on ice surfaces. Surprisingly, they see a non-reversible process as evidenced by first order decay kinetics. The results are then interpreted in terms of surface aggregation due to strong lateral interactions. These results are in stark contrast to previous publications on the interaction of H₂O₂ on ice (Clegg and Abbatt, Pouvesle et al) yet the authors do not make any attempt to either indicate that these differences exist or explain them. Rather they simply state that there is agreement between these studies regarding the temperature and partial pressure dependence of the amount of H₂O₂ uptake. Whilst the results of this study (once properly compared and contrasted to previous work) might be interesting from a physical chemistry or surface science perspective, there is little of interest for atmospheric science as they appear to be working in a concentration regime in which aggregation or condensation of H₂O₂ dominates the uptake. This does not happen in

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the atmosphere and the uptake coefficients they present cannot be used to calculate H₂O₂ loss rates as the true situation is one of reversible uptake defined by a partition coefficient rather than limited by kinetics. It is not obvious why the authors have chosen ACP to publish this study, which is better suited to a physical chemistry journal.

Specific

The introduction consists of a selection of apparently random and partially repetitive sentences describing various environmental phenomena motivating this work. Atmospheric science appears not to be the underlying motivation for this study.

P30093, L16-21 Both Clegg and Abbatt and Pouvesle et al did more than just describe the temperature and partial pressure dependence of the amount of H₂O₂ taken up to the surface. They both showed that the uptake is COMPLETELY REVERSIBLE and derived equilibrium partition coefficients (absorption isotherms).

Pouvesle et al did not report uptake coefficients as this becomes a meaningless (or at best a time dependent) parameter for a reversible interaction. However, from their Figure 1, it is possible to calculate that the initial (experimental) uptake coefficient at 233 K was about 6e-3. As desorption occurs on the time scale of adsorption, this is a lower limit to the initial uptake coefficient to a clean ice surface (which may also be interpreted as a lower limit to the accommodation coefficient).

P30096, L17-22 I think what the authors are trying to say is that they calculated the concentration of H₂O₂ from vapor pressure data for a 93 % H₂O₂ solution. This needs to be rewritten.

P30097 The authors refer to measurement of the “initial” uptake coefficient, yet (if the H₂O₂ signal decays exponentially with injector position as the authors assume) the method can only return a time-independent uptake coefficient. In Figure 5 the authors show that identical uptake profiles are observed when using the same ice film several times. There is thus no evidence for surface saturation in these experiments and there

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cannot be an "initial uptake coefficient".

P30097/98 The authors present the uptake of H₂O₂ on ice in Figure 1. From this Figure it is apparent that only a small change in the H₂O₂ concentration was monitored (a factor of 2-3). Thus it is not proven that the uptake rigorously follows the expected first-order kinetics used for the analysis and extraction of gamma. Secondly, the initial H₂O₂ concentration was stated to be 1.5e-5 Torr, which is equivalent to 8e11 molecule /cm³ at this temperature. Under these conditions, the adsorption isotherms of Pouvesle et al. are in the plateau regime, i.e. the ice surface is saturated with H₂O₂. An exponential decay in H₂O₂ (to calculate gamma) is not expected under these conditions unless the uptake moves from a reversible regime to an irreversible regime due e.g. to formation of a new stable phase.

P30098/99 The uptake coefficient is corrected for pore diffusion into the ice surface layers. The authors claim that the internal surface area of a vapor deposited ice film is "generally accepted". This is however not the case, and there has been much discussion of this (Leu et al., 1997; Hanson and Ravishankara, 1993). The authors have corrected their data by assuming a tortuosity factor of 3.3. The plot of variation of g with ice thickness (Figure 2) is not convincing. Only a single data point at the thinnest ice film indicates some variation with thickness. The corrected result they obtain for g at about 220 K is 6.6e-5 (Table 2). This result is a factor 100 lower than the lower limit (6e-3) calculated above. One could conclude that this correction (which from Table 2 appears to be close to a factor 40) is not appropriate. Alternatively, the low values of g which these authors derive could simply be the result of H₂O₂ desorption during the uptake measurement.

Indeed, the method applied (taking signals at different injector positions) is not appropriate for a system which is known to be reversible. It would have been instructive take a measurement in which the H₂O₂ signal was monitored for an extended period at one injector position to test for reversible behavior.

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P30102, L23 The authors state that the adsorption of a small amount of H₂O₂ on the ice surface does not deactivate it. In fact, from the data of Pouvesle et al, the authors have at least monolayer coverage under their conditions.

P30104, L12 what is the conceptual difference between H₂O₂ in a weakly bound precursor state and physi-sorbed H₂O₂ on an ice surface ?

P30104, L23. The authors state that the amount of H₂O₂ adsorbed on the surface is low (theta < 0.1). How do they calculate this ?. The data of Pouvesle et al suggest that this is not the case and that theta is greater than 0.9 for all the data in this graph (190 K, H₂O₂ 1-5 e-5 Torr).

P30105, L19 The fact that the precursor model (without aggregation) cannot reproduce the results is no surprise. The precursor model would also suggest that the uptake is reversible, which would then imply that the data analysis (measuring time independent, first order loss rates to the surface) is incorrect.

P30106, L24. The authors suggest (again) that coverage is low with 8.9e-6 Torr H₂O₂ at T>190 K. This is not true. The data of Pouvesle et al show that even at the highest temperature, theta is about 0.4.

P30108, L21 The use of alpha to describe net experimental sticking coefficients is discouraged.

P30109, L13 There are no reported uptake coefficients for H₂O₂ on ice surfaces for good reason. The previous studies have found the uptake at atmospheric temperatures to be reversible. However, lower limits to gamma can be calculated (see comment above) and suggest that the values reported here are too low by orders of magnitude.

P30110, L13 A discussion of H₂O₂ lifetimes (e.g. comparing J-values to heterogeneous uptake to ice) based on laboratory measured uptake coefficients for an unexpectedly irreversible interaction is not particularly useful.

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