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## Towards a better understanding of the HO<sub>2</sub> uptake coefficient to aerosol particles measured during laboratory experiments

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The first measurements of HO<sub>2</sub> uptake coefficients ( $\gamma_{\text{HO}_2}$ ) onto suspended aerosol particles as a function of temperature are reported in the range 314 K to 263 K. For deliquesced ammonium nitrate (AN) particles  $\gamma_{\text{HO}_2}$  increases from  $0.005 \pm 0.002$  to  $0.016 \pm 0.005$  as the temperature is lowered over this range. For effloresced sodium chloride and ammonium sulphate particles,  $\gamma_{\text{HO}_2}$  decreases slightly from  $0.004 \pm 0.002$  to  $0.000 \pm 0.002$  and  $0.002 \pm 0.003$ , respectively, between 314 and 263 K. For AN particles doped with Cu<sup>2+</sup> ions, we find  $\gamma_{\text{HO}_2} \approx \alpha_{\text{HO}_2}$ , the mass accommodation coefficient, which increases very slightly from  $\alpha_{\text{HO}_2} = 0.62 \pm 0.05$  to  $0.71 \pm 0.06$  between 292 and 263 K with lowering temperature. New measurements of  $\gamma_{\text{HO}_2}$  are also reported for ammonium sulphate particles doped with a range of Fe<sup>2+</sup> and Fe<sup>3+</sup> concentrations. The dependence of  $\gamma_{\text{HO}_2}$  on Cu and Fe concentrations are reconciled with published rate coefficients using the kinetic multi-layer model of aerosol surface and bulk chemistry (KM-SUB). The model shows that in experimental studies using aerosol flow tubes, a time dependence is expected for  $\gamma_{\text{HO}_2}$  onto aerosol particles which do not contain transition metal ions due to a decrease in the gas-phase concentration of HO<sub>2</sub> as a function of time. The model also demonstrates that Fenton-like chemistry has the potential to decrease  $\gamma_{\text{HO}_2}$  as a function of time for particles containing transition metal ions. For atmospherically relevant transition metal ion concentrations in aerosol particles,  $\gamma_{\text{HO}_2}$  can take a range of values depending on pH and the particle size from  $\gamma_{\text{HO}_2} < 0.04$  to  $\gamma_{\text{HO}_2} = \alpha_{\text{HO}_2}$ .  $\gamma_{\text{HO}_2}$  for larger particles (radius  $\geq 0.5 \mu\text{m}$ ) can be significantly reduced by gas-diffusion limitations.

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### Environmental significance

HO<sub>2</sub> plays a crucial role in the oxidation chemistry of the atmosphere, but the numerical value of its uptake coefficient ( $\gamma_{\text{HO}_2}$ ) that is used in atmospheric modelling remains uncertain. In this study, experiments indicate that  $\gamma_{\text{HO}_2}$  for deliquesced and effloresced particles will increase with decreasing temperature. Literature rate coefficients are included in a kinetic model to better understand measured  $\gamma_{\text{HO}_2}$  trends as a function of time, gas-phase concentrations of HO<sub>2</sub>, and particle-phase concentrations of transition metal ions. The model demonstrates that  $\gamma_{\text{HO}_2}$  can vary significantly for different atmospherically relevant particles, reveals important factors that control  $\gamma_{\text{HO}_2}$ , and identifies further experiments that could be performed to resolve uncertainties.

## 1. Introduction

OH and HO<sub>2</sub> radicals (collectively known as HO<sub>x</sub>) control the oxidative capacity of the troposphere and hence the lifetimes and concentrations of many trace species within the troposphere, such as NO<sub>x</sub> (NO and NO<sub>2</sub>) and volatile organic compounds (VOCs). The reaction of HO<sub>2</sub> with NO is a major

source of ozone, which can damage vegetation, is a respiratory irritant and a greenhouse gas.<sup>1,2</sup> Gas-phase reactions controlling HO<sub>x</sub> concentrations have been extensively studied, and recommendations for rate coefficients, product branching ratios and photochemical parameters such as absorption cross-sections and photolysis quantum yields have been made for the wider community in models by panels of experts.<sup>3-5</sup> Although there is also an IUPAC recommendation for heterogeneous reactions which includes HO<sub>2</sub> uptake to aerosol particles,<sup>6</sup> there remain uncertainties in processes which control the uptake coefficient  $\gamma_{\text{HO}_2}$ . Over more than two decades, measurements during field campaigns, particularly at lower levels of NO<sub>x</sub>, have often shown lower HO<sub>2</sub> concentrations than predicted by box models containing a mechanism for gas-phase reactions and which have been constrained to other measured species.<sup>7-23</sup> The

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overprediction by the models has often been attributed, at least in part, to HO<sub>2</sub> uptake by aerosol particles, although for some earlier studies in coastal regions this conclusion was reached when HO<sub>2</sub> loss *via* reactions with halogen oxides was not recognised and hence not included in the model.

Parameterisations of  $\gamma_{\text{HO}_2}$  for use in atmospheric models have been suggested for a number of modelling studies.<sup>24,25</sup> Modelling studies often use a single value of  $\gamma_{\text{HO}_2} = 0.2$  (e.g. Jacob<sup>26</sup>), and studies using the GEOS-Chem model suggested that increases in ozone levels in China were driven by the decrease in levels of PM<sub>2.5</sub> in response to government legislation, because PM<sub>2.5</sub> scavenges HO<sub>2</sub> which would otherwise react with NO<sub>x</sub> to generate O<sub>3</sub>.<sup>25</sup> Song *et al.*<sup>27</sup> recently developed a new parameterisation for  $\gamma_{\text{HO}_2}$  that depends both on measured concentrations of Cu<sup>2+</sup> within field-sampled aerosol particles and the aerosol liquid water content, the latter calculated from the measured relative humidity (RH). The parameterisation was applied in a multiphase reaction kinetic model, which predicts values of  $\gamma_{\text{HO}_2}$  that varied significantly during a given field campaign, suggesting a single value of  $\gamma_{\text{HO}_2}$  is not appropriate.<sup>27,28</sup> Moreover, several field measurements of HO<sub>2</sub> in China together with modelling studies, some of which utilise this new parameterisation, do not support an important role for heterogeneous uptake of HO<sub>2</sub> except under low concentrations of NO<sub>x</sub>.<sup>27,29</sup> Guo *et al.*<sup>30</sup> reported a theoretical evaluation of the roles of several factors which control  $\gamma_{\text{HO}_2}$  for spherical aerosol particles containing a range of Cu<sup>2+</sup> ion concentrations. The study also showed that the use of a single value of  $\gamma_{\text{HO}_2}$  for aerosol particles of different size, composition or physical state was not appropriate, and concluded that both careful selection of the appropriate value of  $\gamma_{\text{HO}_2}$  should be made for modelling studies and that further laboratory measurements are needed. However, this theoretical analysis is based on a modified resistor model with some limitations; for example, it does not take into account second-order reactions of HO<sub>2</sub> nor the presence of any pH gradient inside of the aerosol particle due to reaction. Similarly, Li *et al.*<sup>31</sup> also recently used a resistor model to investigate the effect of variables such as the HO<sub>2</sub>, Fe and Cu concentrations on  $\gamma_{\text{HO}_2}$  and demonstrated that a wide range of  $\gamma_{\text{HO}_2}$  values were expected.

Taketani *et al.*<sup>32</sup> measured values of  $\gamma_{\text{HO}_2}$  from 0.09–0.40 from regenerated aerosol particles of water extracts from ambient aerosol particles at two mountain sites in China, which together with aerosol composition measurements suggested a key role for transition metals in controlling HO<sub>2</sub> uptake. Recently Zhou *et al.* reported values of  $\gamma_{\text{HO}_2}$  using online HO<sub>2</sub> reactivity measurements under ambient conditions in two Japanese cities with a system that enriches ambient aerosol particles.<sup>33–35</sup> Using an auto-switching aerosol filter, Zhou *et al.* were able to isolate the loss of HO<sub>2</sub> due to heterogeneous uptake, with an average  $\gamma_{\text{HO}_2}$  of 0.24, but displaying considerable variability, and concluding that a single value of  $\gamma_{\text{HO}_2}$  should not be used in modelling studies. Using a chemical transport model, Ivatt *et al.*<sup>36</sup> showed that for some parts of the world the dominant chain termination reaction was not reaction of OH with NO<sub>2</sub> to form nitric acid, nor reaction of RO<sub>2</sub> with HO<sub>2</sub> to form peroxides, but rather the reactive removal of HO<sub>2</sub>

onto aerosol surfaces, placing these regions into a new “aerosol inhibited” photochemical regime.

There are still relatively few laboratory studies that have investigated the  $\gamma_{\text{HO}_2}$  for different types of aerosol particles, with a large variance in the values reported. Small uptake coefficients are reported in some studies for effloresced (solid,  $\gamma_{\text{HO}_2} < 0.004$ ) and deliquesced (aqueous,  $0.004 < \gamma_{\text{HO}_2} < 0.02$ ) aerosol particles containing organic compounds and inorganic salts.<sup>37–39</sup> However, other studies have measured much larger  $\gamma_{\text{HO}_2}$  for these solid ( $\gamma_{\text{HO}_2} < 0.01$ – $0.05$ ) and aqueous ( $\gamma_{\text{HO}_2} = 0.09$ – $0.19$ ) aerosol particles.<sup>39–42</sup> Li *et al.*<sup>31</sup> have recently demonstrated that differences in  $\gamma_{\text{HO}_2}$  between studies may be in part due to different experimental HO<sub>2</sub> concentrations. Lakey *et al.*<sup>43</sup> reported a large difference ( $\sim 4$  orders of magnitude) between rate coefficients of aqueous phase HO<sub>2</sub>/O<sub>2</sub><sup>−</sup> and Cu<sup>+</sup>/Cu<sup>2+</sup> published in the literature,<sup>43,44</sup> and those required to fit  $\gamma_{\text{HO}_2}$  measurements for aerosol particles containing a range of copper ion concentrations. Additional measurements of  $\gamma_{\text{HO}_2}$  as a function of Cu and Fe concentrations have recently been published, demonstrating that Cu must be greater than  $10^{-5}$  M to significantly increase  $\gamma_{\text{HO}_2}$ .<sup>27,31,42</sup> By assuming a low pH  $\sim 4$  and a smaller rate coefficient ( $1.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) between Cu<sup>2+</sup> ions and HO<sub>2</sub>/O<sub>2</sub><sup>−</sup> than had previously been used ( $8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ), studies have been able to reproduce the increasing uptake coefficients with an increase of Cu concentrations.<sup>27,31</sup> Li *et al.*<sup>31</sup> were also able to reproduce an Fe-doped experiment by similarly lowering the rate coefficient between Fe<sup>3+</sup> and HO<sub>2</sub>/O<sub>2</sub><sup>−</sup>. It has been suggested that the lower rate coefficient between Cu<sup>2+</sup> and HO<sub>2</sub>/O<sub>2</sub><sup>−</sup> may reflect the overall rate coefficient expected in more acidic environments.<sup>27,31,45</sup>

A time dependence and a HO<sub>2</sub> concentration dependence of  $\gamma_{\text{HO}_2}$  during some experiments<sup>38,46</sup> have been observed, raising the question of which value should be used within an atmospheric model. A larger value of  $\gamma_{\text{HO}_2}$  was measured at lower HO<sub>2</sub> concentrations, which is inconsistent with the assumption that the uptake is controlled by HO<sub>2</sub> self-reaction within the aerosol particle.<sup>38,47</sup> Thus, there are still uncertainties regarding  $\gamma_{\text{HO}_2}$  in terms of discrepancies between field measurements and model calculations, different laboratory studies and reported rate coefficients of HO<sub>2</sub>/O<sub>2</sub><sup>−</sup> with Cu<sup>+</sup>/Cu<sup>2+</sup> in the aqueous phase.

Previous studies<sup>48–50</sup> measured the uptake coefficient of HO<sub>2</sub> at low total pressure (1–3 torr in He) on dry surfaces or solid films of ammonium nitrate, sodium chloride and bromide, and magnesium chloride over a range of temperatures between 240–345 K, with the uptake coefficient decreasing significantly with increasing temperature. There have also been several studies of  $\gamma_{\text{HO}_2}$  onto sulphuric acid aerosol particles at room temperature<sup>39</sup> as well as onto surfaces coated with sulphuric acid at lower temperatures.<sup>51–53</sup> The  $\gamma_{\text{HO}_2}$  onto sulphuric acid also appeared to be temperature dependent with an uptake coefficient of  $< 0.01$  and  $> 0.2$  measured at 295 K and 243 K, respectively. Field measurements have shown that a larger  $\gamma_{\text{HO}_2}$  is required to explain the difference between measured and predicted HO<sub>2</sub> concentrations at low temperatures.<sup>15,47</sup> However, to the best of our knowledge, currently there is no study



investigating the temperature dependence of  $\gamma_{\text{HO}_2}$  onto suspended deliquesced and effloresced aerosol particles.

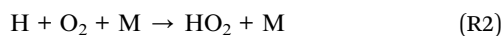
In this paper we report the first systematic measurements of  $\gamma_{\text{HO}_2}$  for effloresced and deliquesced ammonium nitrate, sodium chloride and ammonium sulphate aerosol particles as a function of temperature. Measurements of  $\gamma_{\text{HO}_2}$  for  $(\text{NH}_4)_2\text{SO}_4$  particles containing variable concentrations of  $\text{CuSO}_4$ ,  $\text{FeSO}_4$  and  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$  are also made. In addition, a simplified mechanism for aerosol uptake of  $\text{HO}_2$  incorporated within the kinetic multi-layer model of aerosol surface and bulk chemistry (KM-SUB) is used to examine the chemical and physical processes that control  $\gamma_{\text{HO}_2}$ , to rationalize uncertainties and compare the measurements in this work with earlier studies.<sup>27,31,38–40,42,43</sup>

## 2. Methods

### 2.1. General description of apparatus

Experiments were performed using the setup first described by George *et al.*<sup>38</sup> and used in other studies,<sup>37,43,46,54</sup> and only a brief description is given here. Atomizer solutions used to generate aerosol particles were prepared by dissolving 5 grams of either sodium chloride (Fisher, 99.9%) or ammonium nitrate (Fisher, 99.9%) into 500 ml Milli-Q water. For some experiments, copper sulphate, iron sulphate or ammonium iron sulphate (Fisher 99.8%) was also added to the atomizer solutions. The concentration of copper and iron in the aerosol particles were estimated from the atomizer concentration solutions following the methodology described in Section 2.2. Aerosol particles were generated from these solutions in a flow of  $\text{N}_2$  using an atomizer (TSI 3076), and passed through a neutralizer (Grimm 5522), an impactor (TSI 1035900, 0.071 cm pinhole) and a HEPA (High Efficiency Particulate Air) filter/bypass allowing the particle concentration to be altered. Subsequently, the particle flow ( $1.0 \pm 0.1$  slpm) was mixed with a humidified flow of  $\text{N}_2$  ( $3.0 \pm 0.1$  slpm) in a conditioning flow tube for  $\sim 10$  seconds before entering the reaction flow tube. The size-resolved aerosol particle concentration was measured using a Scanning Mobility Particle Sizer (SMPS, TSI 3080) after the flow tube.

$\text{HO}_2$  radicals were formed by the photolysis of water vapour over a mercury lamp (L.O.T. Oriel, model 6035) in the presence of trace amounts of oxygen as shown below:



The mercury lamp was placed at the end of the injector furthest away from the reaction flow tube to reduce localized heating within the flow tube. The injector flow ( $1.32 \pm 0.05$  slpm), which contained the  $\text{HO}_2$  radicals, was released perpendicularly *via* several small holes into the main flow within the reaction flow tube. At the end of the flow tube, the  $\text{HO}_2$  radicals were sampled by a 1 mm diameter pinhole and entered a Fluorescence Assay by Gas Expansion (FAGE) detector, where they reacted with an excess of added NO to form OH radicals that were then detected by laser induced fluorescence

(LIF) spectroscopy using the  $\text{Q}_1(2)$  transition of the  $A^2\Sigma^+(v' = 0) \leftarrow X^2\Pi_i(v'' = 0)$  band at  $\sim 308 \text{ nm}$ .<sup>20,55</sup> The FAGE detector was kept at low pressure ( $\sim 0.85$  torr) using a combination of a rotary pump (Edwards, model E1M80) and a roots blower (EH1200). The relative  $\text{HO}_2$  LIF signal was converted to an absolute concentration following a calibration with a known concentration of  $\text{HO}_2$ . The initial  $\text{HO}_2$  concentration exiting the moveable injector was varied by altering the current supplied to the mercury lamp and after dilution with the main flow was in the range  $\sim 2.4 \times 10^8 \text{ cm}^{-3}$  to  $\sim 2.7 \times 10^9 \text{ cm}^{-3}$ .

Two experimental methodologies were used to measure the  $\text{HO}_2$  uptake coefficient,  $\gamma_{\text{HO}_2}$ ,<sup>38</sup> referred to as the ‘moving injector’ method and the ‘fixed injector’ method. For ‘moving injector’ experiments, the injector that released the  $\text{HO}_2$  radicals was moved backwards and forwards along the reaction flow tube and the decay of  $\text{HO}_2$  measured both in the absence of and presence of different aerosol particle number concentrations. The decays were performed for reaction times between 10 to 20 seconds, with time zero defined as when  $\text{HO}_2$  is injected into the main flow, allowing time for full mixing. For ‘fixed injector’ experiments the injector was placed in 6 different positions along the flow tube (equivalent to reaction times of  $\sim 5, 8, 11, 14, 17$  and  $20$  seconds) and the  $\text{HO}_2$  signal was measured as the aerosol particle concentration in the flow tube was changed. The main difference between these two methodologies is that for the ‘moving injector’ experiments the measured  $\gamma_{\text{HO}_2}$  is equivalent to the average  $\gamma_{\text{HO}_2}$  for a reaction time between 10–20 seconds, whereas for the ‘fixed injector’ experiments  $\gamma_{\text{HO}_2}$  is equivalent to the average  $\gamma_{\text{HO}_2}$  between 0 seconds (point of mixing of  $\text{HO}_2$  and aerosol particles) and the reaction time corresponding to the fixed position of the injector.

### 2.2. Moving injector experiments

For ‘moving injector’ experiments (which is the methodology used for the majority of  $\text{HO}_2$  aerosol uptake experiments), the  $\text{HO}_2$  decay along the flow tube in the absence and presence of different aerosol particle concentrations was assumed to follow first-order kinetics as follows:

$$\ln[\text{HO}_2]_t = \ln[\text{HO}_2]_0 - k_{\text{obs}}t \quad (\text{E1})$$

where  $[\text{HO}_2]_t$  is the  $\text{HO}_2$  concentration at time  $t$ ,  $[\text{HO}_2]_0$  is the initial  $\text{HO}_2$  concentration and  $k_{\text{obs}}$  is the observed pseudo-first order rate coefficient. In the absence of aerosol particles  $k_{\text{obs}} = k_{\text{wall}}$ . The  $k_{\text{obs}} - k_{\text{wall}}$  rate coefficients were corrected to  $k'$  in order to take into account non-plug flow conditions within the flow tube using the method described by Brown.<sup>56</sup> The Brown correction meant that on average  $k'$  was 35% larger than  $k_{\text{obs}} - k_{\text{wall}}$ . The  $k'$  values were related to  $\gamma_{\text{HO}_2}$  by:

$$k' = \frac{\gamma_{\text{HO}_2} w_{\text{HO}_2}}{4} S \quad (\text{E2})$$

where  $w_{\text{HO}_2}$  is the molecular velocity of  $\text{HO}_2$  and  $S$  is the total aerosol particle surface area. Finally,  $\gamma_{\text{HO}_2}$  was corrected for gas-phase diffusion limitations using the methodology described by Fuchs and Sutugin<sup>57</sup> and this correction changed  $\gamma_{\text{HO}_2}$  by less than 1%.



### 2.3. Fixed injector experiments

For 'fixed injector' experiments the injector was placed in one position at a time and the HO<sub>2</sub> signal was recorded whilst the aerosol particle concentration was varied. The HO<sub>2</sub> signal when aerosol particles were present could be described by the following equation:

$$\frac{\ln[\text{HO}_2]_{t,\text{aerosol}} - \ln[\text{HO}_2]_0}{t} = -k_{\text{aerosol}} - k_{\text{wall}} \quad (\text{E3})$$

where [HO<sub>2</sub>]<sub>0</sub> and [HO<sub>2</sub>]<sub>t,aerosol</sub> are the HO<sub>2</sub> concentration at time zero and at time *t* for a given aerosol particle concentration, respectively. Similarly, the signal without any aerosol particles present can be described as:

$$\frac{\ln[\text{HO}_2]_{t,\text{aerosol}=0} - \ln[\text{HO}_2]_0}{t} = -k_{\text{wall}} \quad (\text{E4})$$

Subtraction of (E3) and (E4) gives:

$$\frac{\ln[\text{HO}_2]_{t,\text{aerosol}} - \ln[\text{HO}_2]_{t,\text{aerosol}=0}}{t} = -k_{\text{aerosol}} \quad (\text{E5})$$

Therefore, for a given injector position, dividing  $\ln[\text{HO}_2]_{t,\text{aerosol}=0} - \ln[\text{HO}_2]_{t,\text{aerosol}}$  by *t* gives a value of *k*<sub>aerosol</sub> for each aerosol particle surface area concentration. The Brown correction was then applied to obtain *k'* and eqn (E2) was used to obtain  $\gamma_{\text{HO}_2}$ , which was then corrected for gas phase diffusion limitations, but as for the moving injector experiments this changed the values by less than 1%.

A range of moving and fixed injector experiments were performed for a range of experimental conditions.

### 2.4. Temperature-dependent experiments of $\gamma_{\text{HO}_2}$

For some experiments the temperature was varied between -10 °C (263 K) and 40 °C (313 K) by flowing a 50 : 50 mixture of water and ethylene glycol, which had been cooled or heated using a refrigerated circulator (Thermo Scientific Haake, DC50-K35), through the jackets of both the conditioning flow tube and the main flow tube. Any axial or radial temperature gradients were measured within the flow tube, both along the top edge next to the jacket and along the centre of the flow tube using moveable thermocouples. As shown in Fig. 1, the temperature gradients are small, within 1 °C for almost the whole flow tube.

Initially, attempts were made to place the entire Differential Mobility Analyser (DMA) in a freezer to maintain its temperature and relative humidity to be same as in the aerosol flow tube. However, temperature gradients developed in the freezer leading to convection within the DMA and no aerosol particles were measured. Therefore, the DMA was always kept at room temperature whilst the temperature in the conditioning and reaction flow tubes was varied. When the flow tube was not at room temperature, the relative humidity within it was different to the relative humidity in the DMA that was always kept at room temperature. When the flow tube was at a temperature that was lower than room temperature, the relative humidity in the flow tube would be greater than in the DMA, and therefore

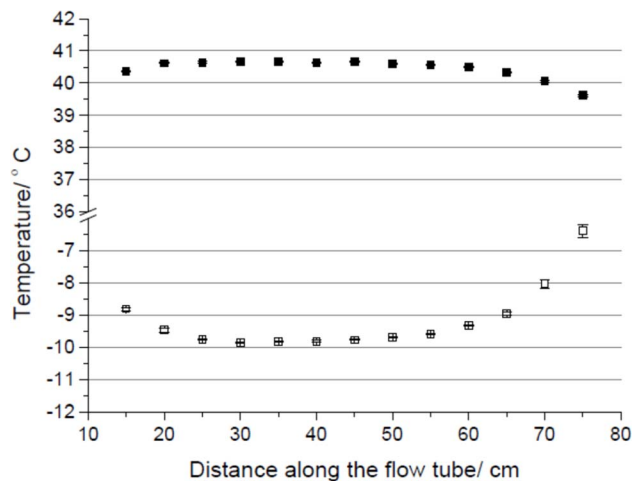


Fig. 1 Temperature gradients along the flow tube when the chiller was set to -10 °C and 40 °C (the two extreme temperatures). The injector tip was radially centered and placed at 75 cm from the end of the flow tube, which was open to the atmosphere at 0 cm. The flows were the same as the flows used during experiments.

the total aerosol particle surface area would be larger in the flow tube than the surface area measured by the SMPS. Alternatively, when the flow tube was at a temperature that was higher than room temperature, the humidity in the flow tube was lower than in the DMA, which meant that the total aerosol particle surface area in the flow tube was smaller than the surface area measured by the SMPS. Therefore, when experiments were performed with aqueous aerosol particles at temperatures different to room temperature, a correction in the total aerosol particle surface area had to be made.

The Extended Aerosol Inorganic Model (E-AIM)<sup>58-60</sup> can calculate the molar volume of an aqueous salt solution as a function of temperature and humidity at thermodynamic equilibrium. This model was run for the conditions in both the aerosol flow tube and the DMA. The following methodology was then used to correct the measured surface area in the SMPS to what it would have been within the aerosol flow tube.

Aqueous aerosol particles were assumed to be spherical and by using E-AIM to obtain the molar volume of an aqueous salt solution at different humidities the fractional change in volume is given by:

$$\frac{V_1}{V_2} = \frac{r_1^3}{r_2^3} \quad (\text{E6})$$

where *V*<sub>1</sub> is the volume for one mole of salt per cubic centimetre at the flow tube temperature and humidity, *V*<sub>2</sub> is the volume for one mole of salt per cubic centimetre at the DMA temperature and humidity. The fractional change in surface area can similarly be given by:

$$\frac{S_1}{S_2} = \frac{r_1^2}{r_2^2} \quad (\text{E7})$$

where *S*<sub>1</sub> is the aerosol particle surface area in the flow tube and *S*<sub>2</sub> is the aerosol particle surface area measured in the DMA.

Therefore, by combining eqn (E6) and (E7), gives:



$$S_1 = S_2 \sqrt[3]{\left(\frac{V_1}{V_2}\right)^2} \quad (\text{E8})$$

Eqn (E8) enables a correction for the total surface area of the aerosol particles when measured at a different humidity to that in the flow tube. For example, for a specific experiment performed using NaCl aerosol particles with the flow tube at 0 °C and the DMA at 20 °C, the relative humidity in the DMA was 18% compared to a relative humidity of 48% in the flow tube. This led to a 15% increase in the aerosol particle surface area measured by the SMPS. The flow rate and volume of the gas within the flow tube was also corrected to take into account the temperature.

It should be noted that the correction to the aerosol particle surface area limited the range of aqueous (deliquesced) aerosol particles that could be investigated to ammonium nitrate, as it does not effloresce over the range of temperatures and relative humidities studied. Deliquesced copper-doped ammonium nitrate aerosol particles appeared to grow or shrink in a similar way to pure ammonium nitrate aerosol particles for a given temperature, so it is assumed that the same growth curve can be applied for doped and non-doped AN. However, this methodology could not be used to apply a correction between effloresced and deliquesced aerosol particles for sodium chloride and ammonium nitrate aerosol particles. Even at 10 °C, to keep the RH in the DMA over the efflorescence humidity of sodium chloride and ammonium nitrate, the RH in the flow tube reactor would have to exceed 100% RH. If the relative humidity in the flow tube exceeded 100% RH there would be condensation on the flow tube walls leading to high wall losses and the aerosol particles would grow to form droplets which would be likely to be deposited and would be too large to be measured by the SMPS. Note that a high relative humidity in the flow tube at an elevated temperature could potentially lead to condensation in the DMA and therefore inaccurate measurements. Below the deliquescence point the aerosol particle surface area does not change with relative humidity for effloresced salts, the surface area remains constant as there is no aqueous phase which can increase or decrease in volume as the humidity changes, and so no surface area correction was required. However, when effloresced salt experiments were performed at different temperatures (ammonium sulphate and sodium chloride), it had to be ensured that the effloresced aerosol particles were never exposed to humidities above their deliquescence point.

The temperature range that was investigated in this work (263–314 K) is relevant for the atmosphere. Measurements have not been made at lower temperatures due to lack of HO<sub>2</sub> sensitivity (due to higher wall losses), larger temperature gradients along the flow tube and droplet formation (since the RH exceeds 100%).

## 2.5. Description of the KM-SUB model

The kinetic multi-layer model of aerosol surface and bulk chemistry (KM-SUB) has previously been described in detail by Shiraiwa *et al.*<sup>61</sup> and the adaptations for HO<sub>2</sub> have also previously been outlined.<sup>54</sup> Therefore, the model is only briefly described below. The KM-SUB model for HO<sub>2</sub> uptake consists of different layers:

a gas phase, a near-surface gas phase, a sorption layer and 100 bulk layers. Processes included within the model are gas-phase diffusion, adsorption and desorption to and from the surface of the aerosol particle, surface-bulk exchange, diffusion between the bulk layers of the aerosol particle as well as chemical reaction in the gas phase, the particle bulk, and on the walls of the flow tube. Each of these processes have been described in detail elsewhere.<sup>61,62</sup> We assumed that the aqueous chemistry shown by reactions (R3)–(R17) below occurred within the aerosol particles. In the model, a gas-phase loss of HO<sub>2</sub> *via* its self-reaction (reaction (R18)) and an uptake of HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> to the walls of the flow tube (Table 1) were included. For simplicity the pH in the aerosol particles was assumed to be constant without being influenced by the following reactions.

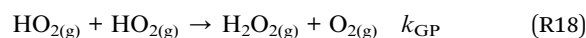
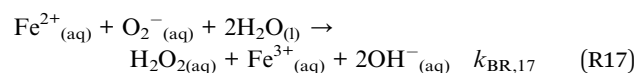
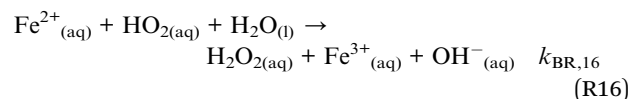
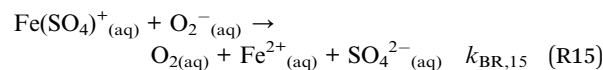
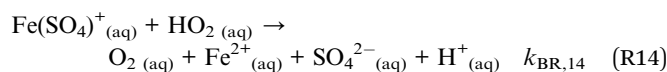
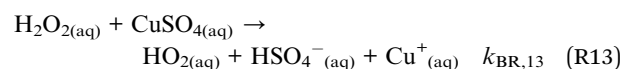
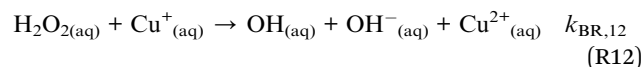
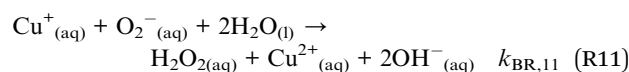
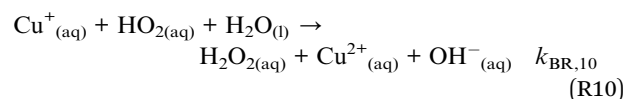
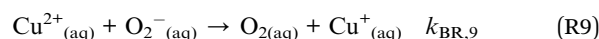
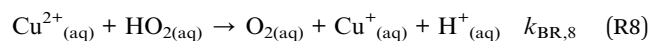
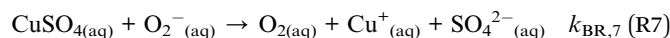
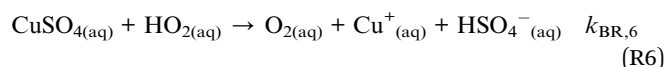
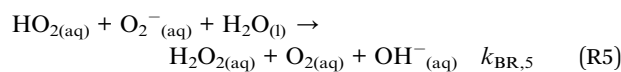
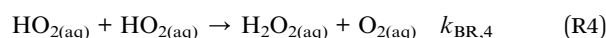
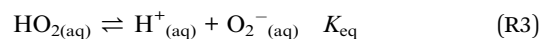


Table 1 The parameters used within the KM-SUB model when fitting all experimental data at 293 K

Parameter	Description	Value	Reference or comment
$K_{\text{eq}}$	Equilibrium constant for reaction (R3)	$2.1 \times 10^{-5}$	Thornton <i>et al.</i> <sup>47</sup>
$k_{\text{BR},4}$	Rate coefficient for reaction (R4)	$1.3 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$	Thornton <i>et al.</i> <sup>47</sup>
$k_{\text{BR},5}$	Rate coefficient for reaction (R5)	$1.5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$	Thornton <i>et al.</i> <sup>47</sup>
$k_{\text{BR},6}^a$	Rate coefficient for reaction (R6)	$1.7 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$	Mao <i>et al.</i> <sup>63</sup>
$k_{\text{BR},7}^a$	Rate coefficient for reaction (R7)	$1.7 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$	Mao <i>et al.</i> <sup>63</sup>
$k_{\text{BR},8}^b$	Rate coefficient for reaction (R8)	$1.7 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$	Jacob <sup>26</sup>
$k_{\text{BR},9}^b$	Rate coefficient for reaction (R9)	$1.3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$	Jacob <sup>26</sup>
$k_{\text{BR},10}$	Rate coefficient for reaction (R10)	$2.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$	Jacob <sup>26</sup>
$k_{\text{BR},11}$	Rate coefficient for reaction (R11)	$1.6 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$	Jacob <sup>26</sup>
$k_{\text{BR},12}$	Rate coefficient for reaction (R12)	$1.2 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$	Deguillaume <i>et al.</i> <sup>64</sup> only included in Fig. 4(d)
$k_{\text{BR},13}$	Rate coefficient for reaction (R13)	$7.6 \times 10^{-19} \text{ cm}^3 \text{ s}^{-1}$	Pham <i>et al.</i> <sup>65</sup> only included in Fig. 4(d) same rate coefficient as for $\text{Cu}^{2+}$ is assumed
$k_{\text{BR},14}$	Rate coefficient for reaction (R14)	$1.7 \times 10^{-18} \text{ cm}^3 \text{ s}^{-1}$	Rush and Bielski <sup>66</sup>
$k_{\text{BR},15}$	Rate coefficient for reaction (R15)	$2.5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$	Rush and Bielski <sup>66</sup>
$k_{\text{BR},16}$	Rate coefficient for reaction (R16)	$2.0 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$	Jacob <sup>26</sup>
$k_{\text{BR},17}$	Rate coefficient for reaction (R17)	$1.7 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$	Jacob <sup>26</sup>
$\gamma_{\text{wall}}$	Uptake coefficient of $\text{HO}_2$ and $\text{H}_2\text{O}_2$ onto the walls of the flow tube	$6.50 \times 10^{-6}$	$\text{HO}_2$ uptake is consistent with the data. An assumption of no products is made
$k_{\text{GP}}$	Rate coefficient for $\text{HO}_2$ self-reaction in the gas phase	$3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$	Sander <i>et al.</i> <sup>67</sup>
$H_{\text{HO}_2}$	Henry's law coefficient for $\text{HO}_2$	$5600 \text{ M atm}^{-1}$	Thornton <i>et al.</i> <sup>47</sup>
$H_{\text{H}_2\text{O}_2}$	Henry's law coefficient for $\text{H}_2\text{O}_2$	$1.65 \times 10^5 \text{ M atm}^{-1}$	Staffelbach and Kok <sup>68</sup>
$D_{\text{b,all}}$	Diffusion coefficient for all species within the aerosol particle bulk	$1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	Thornton <i>et al.</i> <sup>47</sup>
$\alpha_{\text{s},0}$	Surface accommodation coefficient <sup>c</sup> of $\text{HO}_2$ and $\text{H}_2\text{O}_2$	0.5	These values are used unless otherwise stated
$r_{\text{p}}$	Particle radius	50 nm	
$[\text{HO}_2]$	Initial $\text{HO}_2$ concentration	$1 \times 10^9 \text{ cm}^{-3}$	
$\tau_{\text{d}}$	Desorption lifetime	$1.0 \times 10^{-11} \text{ s}$	
$D_{\text{g}}$	Gas phase diffusion coefficient of $\text{HO}_2$ and $\text{H}_2\text{O}_2$ in the gas phase	$0.25 \text{ cm}^2 \text{ s}^{-1}$	Thornton <i>et al.</i> <sup>47</sup>

<sup>a</sup> Note that the rate coefficients for  $\text{CuSO}_4$  with  $\text{O}_2^-/\text{HO}_2$  have not been directly measured and uncertainty remains with regards to their values.

<sup>b</sup> The rate coefficients with free  $\text{Cu}^{2+}$  are only used in Fig. 4(c) and for comparison with  $\text{CuSO}_4$  in Fig. 5(a). <sup>c</sup> The experimentally measured mass accommodation coefficients may be different from the surface accommodation coefficients if there are significant gas-phase diffusion limitations or if  $\text{HO}_2$  diffusing into the bulk becomes a limiting process but should otherwise equal the surface mass accommodation.

The rate coefficients for these reactions as well as other parameters that were included in the model are summarized in Table 1. It should be noted that most published Cu-doped experiments have been performed in ammonium sulphate particles, where sulphate concentrations are expected to be greater than 3 M for all relative humidities that have been investigated.<sup>27,31,39,40,42,43</sup> Such high sulphate concentrations may cause  $\text{Cu}^{2+}$  to form a  $\text{CuSO}_4$  complex, following a published equilibrium constant for this complex formation of 230.<sup>63,69</sup> Accordingly, at >3 M sulphate,  $\text{CuSO}_4$  concentrations should be significantly higher than  $\text{Cu}^{2+}$  concentrations. Thus, we assume that all Cu is present in the form of  $\text{CuSO}_4$  in the model for ammonium sulphate particles and that  $\text{CuSO}_4$  can participate in Fenton-like reactions (reaction (R13)). However, additional measurements are required to confirm that  $\text{CuSO}_4$  is the dominant species in the Cu-doped ammonium sulphate particles modeled in this work and that the equilibrium constant of 230 is valid under the experimental conditions. For the high

sulphate concentrations in the experiments, most  $\text{Fe}^{3+}$  should form the  $\text{Fe}(\text{SO}_4)^+$  and  $\text{Fe}(\text{OH})^{2+}$  complexes.<sup>63</sup> Both complexes are reported to have the same rate coefficient for their reaction with  $\text{O}_2^-$  and, for simplicity, the rate coefficient for the reaction of  $\text{Fe}(\text{SO}_4)^+$  with  $\text{HO}_2$  is used.<sup>63,66</sup> Sensitivity studies indicate that using the higher rate coefficient of  $k_{\text{BR},14} = 2.2 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$  for the reaction of  $\text{Fe}(\text{OH})^{2+}$  with  $\text{HO}_2$  makes a negligible difference for the simulations performed in this work.<sup>63</sup> Other parameters in Table 1 include the Henry's law constants of  $\text{HO}_2$  and  $\text{H}_2\text{O}_2$  ( $H_{\text{HO}_2}$  and  $H_{\text{H}_2\text{O}_2}$ , respectively), the bulk diffusion coefficient of all species ( $D_{\text{b}}$ ), the desorption lifetime of  $\text{HO}_2$  and  $\text{H}_2\text{O}_2$  ( $\tau_{\text{d}}$ ), the surface accommodation coefficient of  $\text{HO}_2$  and  $\text{H}_2\text{O}_2$  onto an adsorbate-free surface ( $\alpha_{\text{s},0}$ ), the gas-phase diffusion coefficient of  $\text{HO}_2$  and  $\text{H}_2\text{O}_2$  ( $D_{\text{g}}$ ), and the radius ( $r_{\text{p}}$ ) and pH of the aerosol particles. Although the model is only applied to liquid particles in this work, it has the potential to be used for solid particles in the future by setting the partitioning coefficient into the bulk to zero. Transition metal



concentrations in Cu or Fe doped ammonium nitrate or ammonium sulphate particles were calculated using the following equation:

[Cu] or [Fe] in the particles =

$$\frac{[\text{AN or AS}] \text{ in the particles} \times [\text{Cu or Fe}] \text{ in the atomizer}}{[\text{AN or AS}] \text{ in the atomizer}} \quad (\text{E9})$$

The concentration of ammonium nitrate (AN) or ammonium sulphate (AS) in the particles was calculated for the flow tube relative humidity and temperature using the E-AIM.<sup>58–60</sup> For simplicity we have not included activity coefficients in the model, but it is worth noting that their inclusion has the potential to decrease uptake coefficients. Concentrations were approximately 180 times higher in the particles than in the atomizer solutions.

KM-SUB outputs two different uptake coefficients. The true uptake coefficient ( $\gamma_{\text{HO}_2}$ ) is calculated using the near surface gas-phase concentration of a HO<sub>2</sub> molecule, whereas the effective uptake coefficient ( $\gamma_{\text{HO}_2,\text{eff}}$ ) is calculated using the (far-surface) gas-phase concentration to derive the collision flux of HO<sub>2</sub> onto the particle surface.<sup>62</sup> Hence,  $\gamma_{\text{HO}_2,\text{eff}}$  implicitly considers gas-diffusion effects and is typically the observable in measurements and an important variable in atmospheric models when no other form of gas-diffusion correction is performed. The near surface-gas phase concentration can be significantly smaller than the gas-phase concentration if there are gas-diffusion limitations, which can be the case for large particles and fast uptake.<sup>62</sup> For most of the modelling performed in this work, the differences between  $\gamma_{\text{HO}_2}$  and  $\gamma_{\text{HO}_2,\text{eff}}$  were negligible and we only report  $\gamma_{\text{HO}_2}$  for simplicity.

In sensitivity tests that used large particles, a difference was observed and separate values for  $\gamma_{\text{HO}_2}$  and  $\gamma_{\text{HO}_2,\text{eff}}$  reported (see the Results section).

### 3. Results

#### 3.1. Temperature-dependent experiments of $\gamma_{\text{HO}_2}$

The HO<sub>2</sub> uptake coefficients as a function of temperature are summarized in Table 2, which also provides more information about the specific conditions of the experiments.

Several studies have measured markedly different HO<sub>2</sub> uptake coefficients onto solid ammonium sulfate surfaces compared to sodium chloride surfaces, which is indicative of different surface interactions with HO<sub>2</sub>.<sup>38,40,52</sup> It is therefore important to make measurements for both compounds which are commonly found in atmospheric particles. For deliquesced aerosol particles, ammonium nitrate (AN) aerosol particles were chosen because they do not effloresce down to humidities of 0% and therefore a correction could be made for their surface area between the flow tube and the DMA (as described in Section 2.4), which will exhibit different relative humidities. Fig. 2(a) shows an example of the pseudo-first order rate coefficients for loss of HO<sub>2</sub>,  $k'$ , onto deliquesced ammonium nitrate aerosol particles as a function of aerosol particle surface area for the two temperatures, at 263 K (RH = 53%, [HO<sub>2</sub>]<sub>0</sub> = 2.8 × 10<sup>8</sup> cm<sup>-3</sup>) and at 312 K (RH = 18%, [HO<sub>2</sub>]<sub>0</sub> = 4.7 × 10<sup>8</sup> cm<sup>-3</sup>). Fig. 2(b) shows measurements of  $\gamma_{\text{HO}_2}$  as a function of temperature for deliquesced ammonium nitrate and effloresced ammonium sulphate and sodium chloride aerosol particles.

The  $\gamma_{\text{HO}_2}$  measurements shown in Fig. 2 and summarized in Table 2, are the first measurements of  $\gamma_{\text{HO}_2}$  for suspended

**Table 2** A summary of  $\gamma_{\text{HO}_2}$  measured using an atmospheric pressure aerosol flow tube over a range of temperatures. The 'moving injector' data analysis methodology was used (see Section 2.2)

Temperature/K	Aerosol particle type	Effloresced or deliquesced	Relative humidity/%	Initial HO <sub>2</sub> concentration/10 <sup>8</sup> cm <sup>-3</sup>	$\gamma_{\text{HO}_2}$
314	Sodium chloride	Effloresced	9	8.9	0.004 ± 0.002
304		Effloresced	25	6.6	0.002 ± 0.003
292		Effloresced	36	9.8	0.004 ± 0.003
284		Effloresced	39	17	0.001 ± 0.002
274		Effloresced	57	6.0	0.001 ± 0.002
263		Effloresced	40	5.3	0.000 ± 0.002
314	Ammonium sulphate	Effloresced	10	10	0.002 ± 0.003
304		Effloresced	13	12	0.003 ± 0.002
292		Effloresced	21	6.9	0.001 ± 0.002
284		Effloresced	39	8.0	0.001 ± 0.001
274		Effloresced	67	2.4	0.000 ± 0.002
263		Effloresced	46	3.0	0.000 ± 0.001
292	Copper doped ammonium nitrate	Deliquesced	33	12	0.62 ± 0.05
284		Deliquesced	33	13	0.71 ± 0.03
275		Deliquesced	42	9.7	0.65 ± 0.03
263		Deliquesced	43	6.1	0.71 ± 0.06
312	Ammonium nitrate	Deliquesced	18	4.7	0.005 ± 0.002
302		Deliquesced	36	9.7	0.007 ± 0.002
292		Deliquesced	45	13	0.005 ± 0.001
284		Deliquesced	50	12	0.007 ± 0.003
275		Deliquesced	52	6.1	0.010 ± 0.002
263		Deliquesced	53	3.8	0.016 ± 0.005



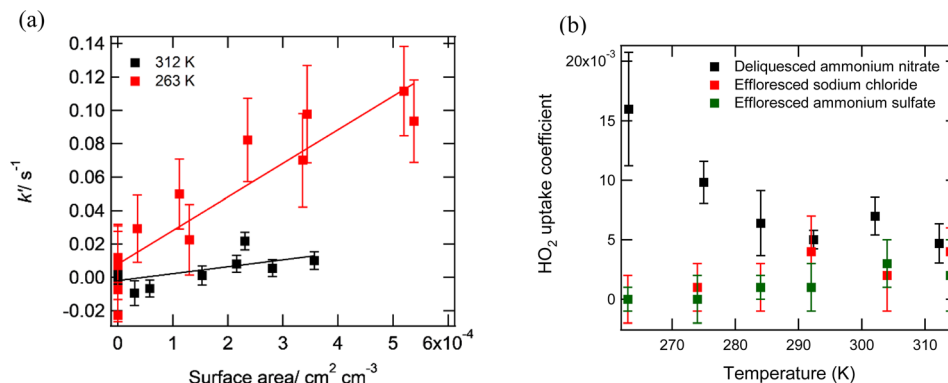


Fig. 2 Panel (a)  $k'$  as a function of the surface area per unit concentration of ammonium nitrate aerosol particles at two different temperatures ( $T = 312$  K, RH = 18%, initial  $[\text{HO}_2] = 4.7 \times 10^8 \text{ cm}^{-3}$ ;  $T = 263$  K, RH = 53%; initial  $[\text{HO}_2] = 3.8 \times 10^8 \text{ cm}^{-3}$ ) and linear fits to experimental data; panel (b) measured  $\gamma_{\text{HO}_2}$  as a function of temperature for deliquesced ammonium nitrate, effloresced sodium chloride and effloresced ammonium sulphate aerosol particles. See Table 2 for conditions of these experiments. The errors represent two standard deviations of between 2 and 8 replicate experiments.

deliquesced or effloresced aerosol particles as a function of temperature. The  $\gamma_{\text{HO}_2}$  increases significantly as the temperature decreases for deliquesced ammonium nitrate particles, which is consistent with the trend in the work by Thornton *et al.*<sup>47</sup> Although the rate coefficients (R4) and (R5) are likely to increase with increasing temperatures, the Thornton *et al.*<sup>47</sup> model demonstrated that the effect of the Henry's law constant dominates over the rate coefficients to decrease  $\gamma_{\text{HO}_2}$  as the temperature increases. Therefore, with increasing temperature, the decrease in the  $\gamma_{\text{HO}_2}$  is the expected behaviour in deliquesced particles due to a smaller HO<sub>2</sub> concentration in the bulk of the aerosol particle and available for self-reaction.

Although there are currently no measured  $\gamma_{\text{HO}_2}$  onto aerosol particles over a range of temperatures reported in the literature, several different studies have measured  $\gamma_{\text{HO}_2}$  onto aqueous sulphuric acid surfaces at low temperatures and onto aqueous sulphuric acid aerosol particles at room temperature. The  $\gamma_{\text{HO}_2}$  was measured to be  $< 0.01$  at 295 K,<sup>39</sup>  $> 0.05$  at 249 K,<sup>53</sup>  $> 0.2$  at 243 K (ref. 52) and  $0.055 \pm 0.020$  at 223 K.<sup>51</sup> Overall, there appears to be an increase in  $\gamma_{\text{HO}_2}$  with decreasing temperature. However, no study has systematically measured  $\gamma_{\text{HO}_2}$  over a range of temperatures. Griffiths and Cox<sup>70</sup> measured N<sub>2</sub>O<sub>5</sub> uptake coefficients between 263 and 303 K onto aqueous ammonium sulphate and aqueous ammonium bisulphate aerosol particles at a relative humidity of 50%. The uptake coefficients varied from  $0.005 \pm 0.002$  at 303 K to  $0.036 \pm 0.002$  at 263 K for ammonium sulphate and from  $0.003 \pm 0.001$  at 303 K to  $0.036 \pm 0.009$  at 263 K for ammonium bisulphate.

The copper(I and II) and iron(II and III) concentrations in the atomiser solutions for all experiments were measured using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and it was found that although all solutions did contain trace metal contamination, the concentrations were less than 5 ppb. The estimated copper(II) molarity in the aerosol particles was always less than  $5 \times 10^{-5}$  M for both copper(I and II) and iron(II and III) over the range of temperatures and humidities used. As shown in Section 3.3 below, the observed  $\gamma_{\text{HO}_2}$  should therefore not be affected by these levels of trace metals, and trace metals can be ruled out as an explanation for the difference between the

measurements in this work and those predicted by the Thornton *et al.*<sup>47</sup> model. The limiting factors for HO<sub>2</sub> uptake into non-copper doped aqueous ammonium nitrate aerosol particles is likely therefore to be solubility and the rate of reaction of HO<sub>2</sub>, both of which are temperature dependent.

As shown in Fig. 2(b) and Table 2, a slight increase in  $\gamma_{\text{HO}_2}$  with temperature is observed for the effloresced sodium chloride and ammonium sulphate particles, with  $\gamma_{\text{HO}_2}$  increasing from  $0.000 \pm 0.001$  to  $0.004 \pm 0.003$ . However, some of the dependence may be due to a decrease in the relative humidity at higher temperatures (see Table 2 for details of experimental conditions), as it was not possible to keep the RH constant over the range of temperatures used as the flow tube and the DMA were at different temperatures. Measurements have previously shown that the presence of water vapor can block reactive sites on a solid surface and lead to a decrease in  $\gamma_{\text{HO}_2}$ .<sup>71</sup> Other factors, such as HO<sub>2</sub> concentration affecting the uptake measured for these experiments, are also possible. We return to the effect of HO<sub>2</sub> concentration in Section 3.2. below. In contrast to this work, Remorov *et al.*<sup>71</sup> and Loukhovitskaya *et al.*<sup>72</sup> observed a negative temperature dependence for HO<sub>2</sub> uptake to solid coatings of sodium chloride with larger  $\gamma_{\text{HO}_2}$  at lower temperatures. The mass accommodation ( $\alpha_{\text{HO}_2}$ ) is likely to be temperature dependent as will be discussed below for copper doped aerosol particles. Both Remorov *et al.*<sup>71</sup> and Loukhovitskaya *et al.*<sup>72</sup> worked at 0% RH. However, when Remorov *et al.*<sup>71</sup> increased the water vapour in their flow tube from  $[\text{H}_2\text{O}] = 0$  molecule per cm<sup>3</sup> to  $[\text{H}_2\text{O}] = 3 \times 10^{15}$  molecule per cm<sup>3</sup> the uptake coefficient decreased by 13 and 21% at 295 K (RH  $\sim 0.5\%$ ) and 243 K (RH  $\sim 28\%$ ), respectively. Therefore, the lower  $\gamma_{\text{HO}_2}$  at lower temperatures observed in this work may be due to the higher relative humidities that were utilised, meaning that this work is not inconsistent with the work by Remorov *et al.*<sup>71</sup> and Loukhovitskaya *et al.*<sup>72</sup>

The mass accommodation coefficient,  $\alpha_{\text{HO}_2}$ , onto aerosol particles is also expected to be dependent upon temperature. As for previous work, doping with aerosol particles with sufficient Cu(II) means that the uptake of HO<sub>2</sub> is not limited by aqueous chemistry, rather by mass accommodation, and hence



a measurement of  $\gamma_{\text{HO}_2}$  yields  $\alpha_{\text{HO}_2}$ . Table 2 shows the results and also gives the conditions for measurements of the temperature dependence of the mass accommodation  $\alpha_{\text{HO}_2}$  as a function of temperature for copper(II)-doped ammonium nitrate aerosol particles. The aerosol particle copper(II) concentration was estimated as  $\sim 0.7$  M, for which the lifetime of  $\text{HO}_2$  within the aerosol particle is around 100 nanoseconds. It shows that the mass accommodation increases very slightly from  $\alpha_{\text{HO}_2} = 0.62 \pm 0.05$  to  $0.71 \pm 0.06$  between 292 and 263 K which is consistent with known theory about the dynamics and kinetics of the gas–liquid interfaces. Bulk mass accommodation is expected to be temperature dependent following an Arrhenius-type relationship in which the Gibbs free energy barrier of the transition state between the gaseous and solvated phases,  $\Delta G_{\text{soliv}}$ , governs the temperature dependence of the process.  $\Delta G_{\text{soliv}}$  is usually negative for small molecules on aqueous solutions, hence leading to higher accommodation coefficients at lower temperatures.<sup>73</sup> This is in part due to the strong temperature dependence of desorption and reversible adsorption, respectively, which are central to interfacial transport and gas-particle exchange.<sup>74</sup>

Due to the variability in the conditions of the experiments (e.g. RH, wall loss and  $\text{HO}_2$  concentration) and a large number of parameters (e.g. rate coefficients, Henry's law constants) required for the KM-SUB model where the temperature dependence is unknown, we did not attempt to calculate the temperature dependence of  $\gamma_{\text{HO}_2}$  with the model for comparison with experiments.

### 3.2. Dependence of $\gamma_{\text{HO}_2}$ on reaction time and $\text{HO}_2$ concentration

Fig. 3 shows an example of the measured pseudo-first-order rate coefficient for the loss of  $\text{HO}_2$ ,  $k'$ , as a function of aerosol particle surface area for deliquesced sodium chloride aerosol particles at 59% RH and  $T = 293$  K for different reaction times using the fixed injector methodology. From eqn (E2), the

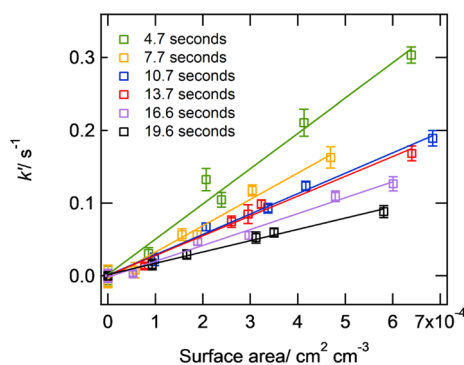


Fig. 3  $k'$  as a function of the surface area per unit concentration of deliquesced sodium chloride aerosol particles at 59% RH and  $293 \pm 2$  K, and for an initial  $\text{HO}_2$  concentration at time zero of  $2.1 \times 10^9$  molecule per  $\text{cm}^3$  for a variety of reaction times (injector position varying from 20–70 cm along the flow-tube) using the 'fixed injector' methodology. The solid lines represent linear-least squares fits to the data (eqn (2)). The error bars represent one standard deviation.

gradient is proportional to  $\gamma_{\text{HO}_2}$ , and it is evident from Fig. 3 that  $\gamma_{\text{HO}_2}$  decreases for larger reaction times.

Fig. 4(a) shows 'moving injector' measurements and modelling of the  $\text{HO}_2$  uptake coefficient as a function of the initial flow tube  $\text{HO}_2$  gas-phase concentration. The model predicts that  $\gamma_{\text{HO}_2}$  will increase with increasing  $\text{HO}_2$  concentrations and should be proportional to  $[\text{HO}_2]_{\text{g}}$  unless it becomes large enough to be limited by mass accommodation. This relationship has previously been described in Thornton *et al.*<sup>47</sup> and a brief explanation follows. The  $\gamma_{\text{HO}_2}$  can be calculated as the net adsorption flux divided by the collision flux. Unless limited by mass accommodation, the adsorption flux should be controlled by reaction and therefore it is proportional to  $k_{\text{BR},4}[\text{HO}_2]^2 + k_{\text{BR},5}[\text{HO}_2][\text{O}_2^-]$ . The collision flux is proportional to  $[\text{HO}_2]_{\text{g}}$ , resulting in  $\gamma_{\text{HO}_2}$  being proportional to  $[\text{HO}_2]_{\text{g}}$ . However, overall measurements collated from several studies do not appear to follow any trend and are quite scattered. Calculations performed using E-AIM suggest that  $(\text{NH}_4)_2\text{SO}_4$  particles should have a  $\text{pH} \leq 4$ . Measurements were significantly higher than those predicted using the model suggesting that perhaps the pH was higher than expected or that trace metal contamination played a role in increasing  $\gamma_{\text{HO}_2}$  which will be explored further in Fig. 4(c) below. The measurement by Thornton and Abbatt at a high  $[\text{HO}_2]_{\text{g}}$  and with a particle buffered to  $\text{pH} = 5.1$  was close to the modelled value. In contrast, most measurements with NaCl particles were smaller than the expected  $\gamma_{\text{HO}_2}$  for particles with a  $\text{pH} = 7$ , which may be partly due to the  $\text{HO}_2$  concentrations along the flow tube being lower than the initial  $\text{HO}_2$  concentration due to wall loss, gas-phase reactions, and uptake to particles. Changes in  $[\text{HO}_2]_{\text{g}}$  were not considered in the modelling of this figure and will be explored below.

Fig. 4(b–d) show examples of  $\gamma_{\text{HO}_2}$  time dependence which were measured using the 'fixed injector' methodology for different aerosol particle compositions and conditions. For all examples,  $\gamma_{\text{HO}_2}$  decreases as a function of time. The kinetic model predicts this behaviour for particles that do not contain transition metals (Fig. 4(b and c)) and is able to reproduce the measured trends and the measurements within a factor of two for uptake to NaCl particles by accounting for  $\text{HO}_2$  loss along the flow tube. Gas-phase reactions, wall losses and uptake to particles account for 1–4%, 10–79% and 17–89% of the total  $\text{HO}_2$  loss, respectively, for the simulations shown in Fig. 4(b). Lower  $\text{HO}_2$  concentrations lead to lower uptake coefficients in the absence of metals as  $\gamma_{\text{HO}_2}$  is controlled by the aqueous self-reactions of  $\text{HO}_2$  (reactions (R4) and (R5)) as discussed above.

The kinetic model predicts that  $\gamma_{\text{HO}_2}$  would be higher if the initial  $\text{HO}_2$  concentration is higher, but the opposite trend is observed in measurements (Fig. 4(b)). Although the reason for the trend in the measurements remains uncertain, model sensitivity tests indicate that there are many factors that could influence the  $\text{HO}_2$  concentration along the flow tube and could potentially skew the uptake coefficient at a given time. For example, variability between experiments such as larger wall losses and higher particle concentrations can cause a reduction in the  $\text{HO}_2$  concentration and uptake coefficient. The kinetic model indicated that changing the concentration of the



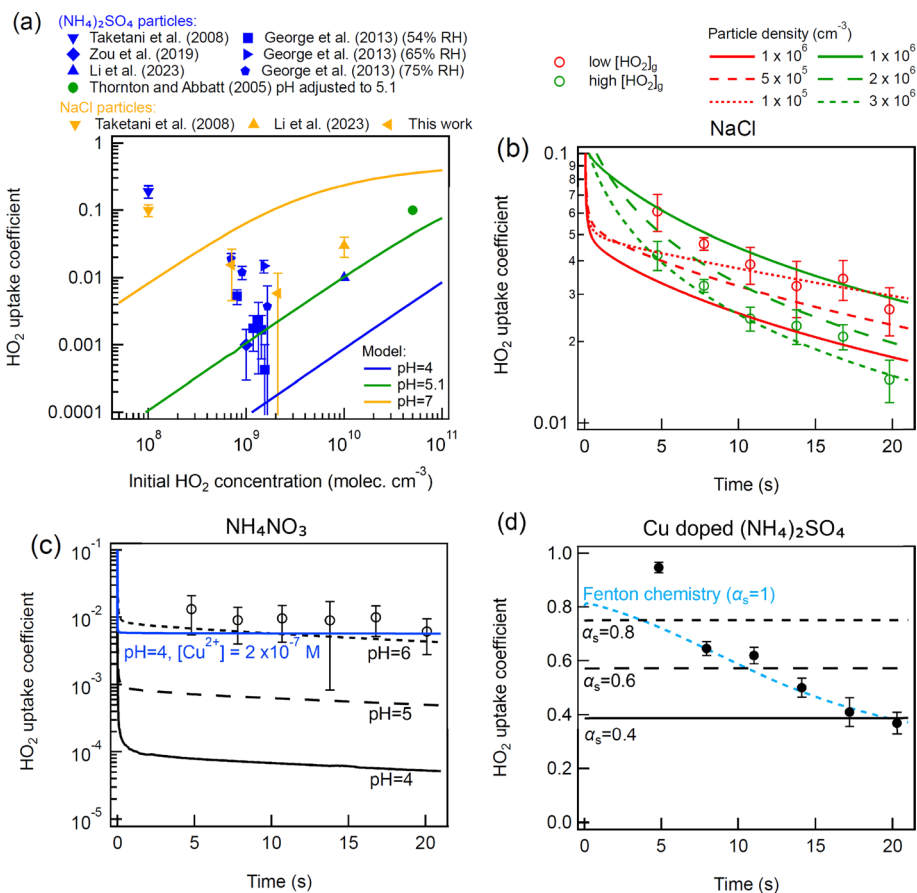


Fig. 4 Panel (a): measurements (markers) and modelling (lines) of  $\gamma_{HO_2}$  as a function of HO<sub>2</sub> concentration and pH for (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> particles and NaCl particles. Measurements were performed using the 'moving injector' methodology. Panels (b–d): measurements (markers) and kinetic modelling (lines) of  $\gamma_{HO_2}$  as a function of time using the 'fixed injector' methodology. Experiments in panel (a) were performed with NaCl particles and initial HO<sub>2</sub> concentrations of  $2.1 \times 10^9$  cm<sup>-3</sup> (green) and  $7.1 \times 10^8$  cm<sup>-3</sup> (red). The experiment in panel (c) was conducted with NH<sub>4</sub>NO<sub>3</sub> particles and an initial HO<sub>2</sub> concentration of  $1 \times 10^9$  cm<sup>-3</sup>. The experiment in panel (d) was conducted using Cu doped (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> particles and an initial HO<sub>2</sub> concentration of  $2.7 \times 10^9$  cm<sup>-3</sup>. NaCl particles are assumed to have a pH of 7 and Cu doped (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> particles are assumed to have a pH of 4. Model simulation parameters are shown in Table 1. Measurements in panel (d) have previously been shown in George *et al.*<sup>58</sup> (2013). In panel (a) a constant [HO<sub>2</sub>]<sub>g</sub> is assumed, while in panels (b–d) HO<sub>2</sub> decreases along the flow tube. In panel (d) the black lines represent the modelled uptake coefficient in the absence of Fenton chemistry for particles containing [Cu(SO<sub>4</sub>)] = 0.6 M while the dashed blue line assumes that Fenton-like chemistry is occurring with an initial H<sub>2</sub>O<sub>2</sub> concentration of  $2 \times 10^{12}$  cm<sup>-3</sup>, a particle number density of  $10^5$  cm<sup>-3</sup> and a H<sub>2</sub>O<sub>2</sub> uptake coefficient to the walls of  $6.5 \times 10^{-6}$ .

particles could lead to the trends observed during the measurements (Fig. 4(b)). Alternatively, it can be speculated that setting the lamp in the injector to a higher power to obtain higher initial HO<sub>2</sub> concentrations may lead to slightly higher initial temperatures resulting in a lower HO<sub>2</sub> partitioning coefficient and different initial mixing conditions. More H<sub>2</sub>O<sub>2</sub> is also expected to exit the injector at higher HO<sub>2</sub> concentrations which could potentially be converted back to HO<sub>2</sub> by Fenton chemistry if there are trace transition metal contaminants in the particles, thereby effectively reducing  $\gamma_{HO_2}$ . Note that although the ICP-MS measurements indicated low metal contamination, any contamination would become enhanced in the concentrated particles, and we cannot fully disregard contamination from impacting  $\gamma_{HO_2}$ . However, the cause of the measured HO<sub>2</sub> concentration dependence remains uncertain and warrants further investigation in the future.

Fig. 4(c) shows time dependent measurements of  $\gamma_{HO_2}$  for ammonium nitrate particles. The overall trend in the uptake coefficients as a function of time is similar to NaCl particles but  $\gamma_{HO_2}$  are significantly smaller. Ammonium nitrate aerosol particles have a lower pH than NaCl aerosol particles which causes the slower reaction (R4) to become more important compared to reaction (R5) and leads to less overall partitioning of HO<sub>2</sub> into the particles (reaction (R3)). Calculations performed with the E-AIM model suggest that the pH of the ammonium nitrate particles should have been <4.<sup>58–60</sup> However, with a pH of 4 the model underestimates  $\gamma_{HO_2}$  measurements significantly. Further sensitivity tests indicated that the measurements could be reproduced if contaminants increased the pH to 6 or if there was a small amount of transition metal contamination (*e.g.* [Cu<sup>2+</sup>]  $\sim 2 \times 10^{-7}$  M) which could be consistent with ICP-MS measurements. Note that uncertainty remains with regards to the formation of Cu complexes in ammonium nitrate particles



and free Cu ion rate coefficients have been assumed for this simulation.

Fig. 4(d) shows an example of the significant time dependence of  $\gamma_{\text{HO}_2}$  for copper-doped ammonium sulphate particles. For these particles, the kinetic model predicts that there should be no time dependence in the experiments and that  $\gamma_{\text{HO}_2}$  should be approximately the same as the surface mass accommodation coefficient (Fig. 4(d)). This discrepancy between the model and the measurements could be due to and influenced by a variety of factors. Firstly, we cannot exclude the possibility that uneven mixing in the initial part of the flow tube, in the region before laminar flow is achieved, could be causing the measured initial high uptake coefficients. An alternative explanation that has been explored with the model is that Fenton-like chemistry may be occurring.  $\text{H}_2\text{O}_2$  is formed in the injector from the self-reaction of  $\text{HO}_2$ . As the ratio of  $\text{HO}_2:\text{H}_2\text{O}_2$  decreases along the flow tube,  $\text{HO}_2$  formation from Fenton-like chemistry becomes more important and the uptake coefficient decreases. Sensitivity tests indicated that the measurements were able to be reproduced well by assuming an initial  $\text{H}_2\text{O}_2$  concentration of  $2.5 \times 10^{12} \text{ cm}^{-3}$ , a particle number density of  $10^5 \text{ cm}^{-3}$  and a  $\text{H}_2\text{O}_2$  uptake coefficient to the walls of  $6.5 \times 10^{-6}$  (same value as for  $\text{HO}_2$ ) (Fig. 4(d)). However, further measurements and more complex modelling are required to better understand these trends and to determine whether Fenton-like chemistry is important in these experiments. It should also be noted that an assumption has been made that  $\text{CuSO}_4$  reacts with  $\text{H}_2\text{O}_2$  in a similar way and with the same rate coefficient as  $\text{Cu}^{2+}$  reacting with  $\text{H}_2\text{O}_2$ . A different rate coefficient would impact the  $\text{H}_2\text{O}_2$  concentration required to fit the measurements. Guo *et al.*<sup>30</sup> determined the impact of the aqueous production of  $\text{HO}_2$  on the uptake coefficient. They concluded that the aqueous-phase production of  $\text{HO}_2$  is an important factor that influences  $\gamma_{\text{HO}_2}$ . However, they did not elaborate which reactions exactly could be responsible for such production. In this work, we are proposing Fenton and Fenton-like chemistry as a possible route, at least in the experimental conditions, to explain this reformation of  $\text{HO}_2$ .

### 3.3. Dependence of $\gamma_{\text{HO}_2}$ on the Cu and Fe concentration

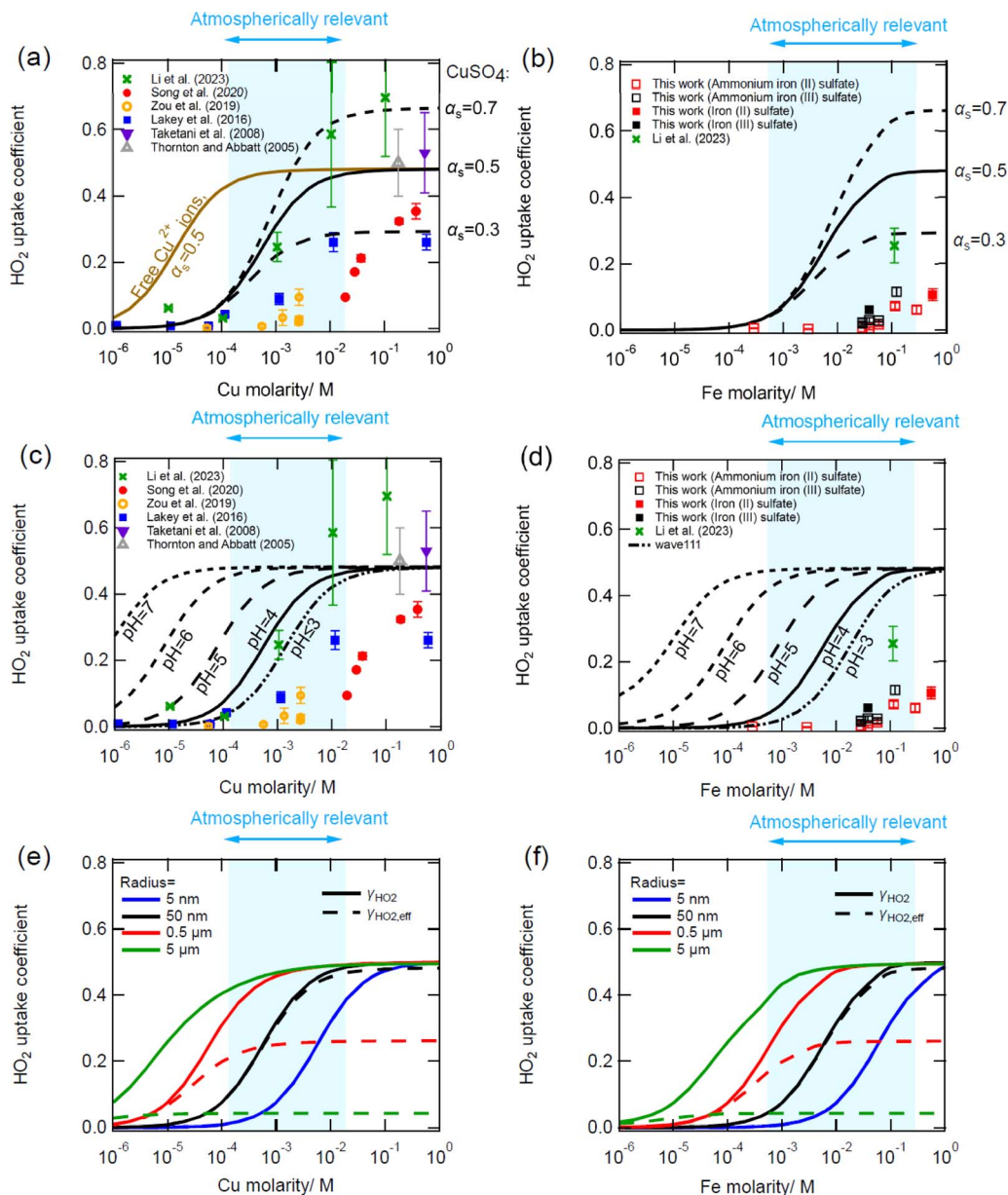
Fig. 5(a) and (b) show measurements from different studies of  $\gamma_{\text{HO}_2}$  as a function of Cu and Fe concentrations, respectively, as well as kinetic modelling results. The kinetic model can fit the measurements for Cu doped aerosol particles relatively well with literature rate coefficients if we assume that all Cu is present as  $\text{CuSO}_4$ . The slower rate coefficients of  $\text{CuSO}_4$  with  $\text{HO}_2/\text{O}_2^-$  compared to  $\text{Cu}^{2+}$  with  $\text{HO}_2/\text{O}_2^-$  assumed in this work lead to lower  $\gamma_{\text{HO}_2}$  than if free  $\text{Cu}^{2+}$  ions were present in the particles (brown line, Fig. 5(a)). Note that for the free  $\text{Cu}^{2+}$  simulation,  $\gamma_{\text{HO}_2}$  is mainly controlled by the fast reactions of  $\text{Cu}^{2+} + \text{O}_2^-$  and  $\text{Cu}^+ + \text{HO}_2/\text{O}_2^-$  and that decreasing the rate coefficient of  $\text{Cu}^{2+} + \text{HO}_2$  has a negligible impact on  $\gamma_{\text{HO}_2}$  at  $\text{pH} = 4$ . It is necessary to vary the surface accommodation coefficient to obtain a good fit to different datasets (Fig. 5(a)). The varying measured mass accommodation coefficients are most likely an experimental artefact which may be due to mixing

conditions, Fenton-like chemistry (as discussed above), activity coefficients (which are not treated in the model) or some other currently unknown process or reaction. A trend in the uptake coefficient onto Cu-doped aerosol particles as a function of relative humidity has been previously described although the reasons for this remain unclear.<sup>42</sup> It should be noted that the Song *et al.*<sup>27</sup> measurements, which the model does not reproduce, are performed at the lowest relative humidity of the different studies ( $\sim 43\%$  RH). The model overestimates the uptake coefficient for Fe-doped particles (Fig. 5(b)), which may be due to Fe precipitation. Significant precipitation of iron was observed in the atomizer solutions one day after they were prepared in this work, which could also be occurring in the concentrated aerosol particles reducing its availability for reaction. Although the chemical formula of the precipitate has not been ascertained, it could be  $\text{Fe}(\text{OH})_2$  or  $\text{Fe}(\text{OH})_3$ . Trace organics have also been shown to have the potential to reduce  $\gamma_{\text{HO}_2}$  onto Cu-doped aerosol particles.<sup>43</sup> Note that sensitivity tests indicate that for atmospherically relevant copper concentrations, the uptake coefficient is independent of  $[\text{HO}_2]_{\text{g}}$  when  $[\text{HO}_2]_{\text{g}}$  is less than  $1 \times 10^{11} \text{ cm}^{-3}$ .

Fig. 5(c) and (d) show the same experimental measurements but with kinetic modelling pH sensitivity test results for atmospherically relevant aerosol particle pH values. Fitting results to measurements indicate that aerosol particles used in the experimental measurements are most likely to exhibit a  $\text{pH} \leq 4$ , which is consistent with ammonium sulphate particles doped with copper and is also consistent with previous modelling work.<sup>27,31</sup> Increasing the pH leads to higher uptake coefficients as the  $\text{HO}_2$  dissociates to form  $\text{O}_2^-$  and the effective partitioning coefficient into the particles increases. Changes in pH also lead to a change in the  $\text{O}_2^-$  to  $\text{HO}_2$  ratio resulting in a different overall rate of destruction (reactions (R6), (R7), (R14) and (R15)). However, decreasing the pH below 3 has a negligible effect for Cu-doped particles as  $\text{HO}_2$ , which has a  $\text{pK}_a$  of 4.7, is already almost entirely protonated and reaction (R6) dominates over reaction (R7).<sup>26</sup> For the equivalent Fe reactions, there is a much larger difference between  $k_{\text{BR},14}$  and  $k_{\text{BR},15}$  leading to reaction (R15) controlling the uptake even at a low pH of 3.

The blue shaded area in Fig. 5 represents a typical range of total soluble iron and copper concentrations measured in different locations and cities in  $\text{PM}_{2.5}$  (Fe: 0.003–1.5% soluble mass fraction, Cu: 0.0008–0.11% soluble mass fraction<sup>75</sup>). For aerosol particles with a 50 nm radius shown in Fig. 5(c and d),  $\gamma_{\text{HO}_2}$  can be equal to a wide range of values in these Cu and Fe concentration ranges, depending on the actual soluble transition metal concentration and the pH. Note that the soluble Cu and Fe concentrations may be different for these smaller particles, but far fewer measurements exist compared to  $\text{PM}_{2.5}$ .<sup>76–78</sup> As of now measurements have been performed on ammonium sulphate particles but future measurements of  $\gamma_{\text{HO}_2}$  as a function of Cu and Fe concentrations should be performed for a wide range of particle compositions for the best comparison with atmospherically relevant concentrations and to gain a better understanding of how the particle composition can influence measurements. It should also be noted that the reaction of  $\text{Cu}^+ + \text{O}_2 \rightarrow \text{Cu}^{2+} + \text{O}_2^-$  has not been included in the model simulations as many





**Fig. 5** Measurements (markers) and modelling (lines) of  $\gamma_{\text{HO}_2}$  as a function of (a, c and e) Cu molarity and (b, d and f) Fe molarity in AS particles. Fe experiments in this work were performed at  $293 \pm 2$  K and  $66 \pm 2\%$  RH. Panels (a and b) show model sensitivity tests for different surface mass accommodations. Panels (c and d) show model sensitivity tests as a function of pH. Panels (e and f) show model sensitivity tests as a function of particle radius. Model simulations are run with a constant HO<sub>2</sub> concentration of  $1 \times 10^9 \text{ cm}^{-3}$ ,  $\alpha_s = 0.5$ , pH = 4 and with a particle radius of 50 nm unless otherwise stated. The atmospherically relevant molarities of soluble iron ( $5.4 \times 10^{-4}$ –0.27 M) and copper ( $1.3 \times 10^{-4}$ –0.018 M) in PM<sub>2.5</sub> particles are shown by the blue shaded area.

experiments were performed under nitrogen. Sensitivity studies indicate that the inclusion of this reaction with a rate coefficient of  $7.6 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$  would lower the HO<sub>2</sub> uptake coefficient by approximately 16–18% when  $[\text{Cu}] \leq 10^{-3} \text{ M}$  for particles with pH = 4.<sup>63,79</sup> For higher Cu concentrations the reduction in the HO<sub>2</sub> uptake coefficient becomes smaller and with a concentration of 1 M the HO<sub>2</sub> uptake coefficient is only reduced by approximately 1%. Additional reactions could also be included in future versions of the model.<sup>63</sup>

Fig. 5(e–f) demonstrate the importance of aerosol particle size on  $\gamma_{\text{HO}_2}$ . As the aerosol particle radius increases,  $\gamma_{\text{HO}_2}$  (calculated

with the near surface gas-phase HO<sub>2</sub> concentration) also increases due to larger volumes in which the reaction can occur for a given surface area. However, the effective  $\gamma_{\text{HO}_2}$  (calculated with the HO<sub>2</sub> gas-phase concentration), which includes gas-phase diffusion limitations, is likely to be significantly reduced. For example, for 5 μm particles the effective uptake coefficient is predicted to be ~0.04 over the atmospherically relevant Cu concentration range. This is consistent with a low Knudsen number of 0.034 for this particle radius, which according to gas-kinetic theory will cause a decrease in the near-surface gas concentration, leading to a significant decrease in the effective



uptake coefficient in the atmospherically relevant range of transition metal concentrations.<sup>62</sup> It should also be noted that for the simulations discussed above, no bulk diffusion limitations due to viscous particles or metal complexation is treated, but these factors have previously been studied and shown to have the potential to reduce  $\gamma_{\text{HO}_2}$  significantly for particles containing high transition metal concentrations.<sup>43,54</sup>

## 4. Discussion and outlook

Our measurements suggest that temperature has a large impact on  $\gamma_{\text{HO}_2}$ , which is consistent with previous parameterizations and known theoretical frameworks.<sup>15,73</sup> However, we are currently unable to constrain these measurements with our KM-SUB model due to the large number of uncertainties including the effect of temperature on the rate coefficients and Henry's law constants.

The KM-SUB model has demonstrated that a time dependence of  $\gamma_{\text{HO}_2}$  is expected in flow tube experiments for particles that do not contain transition metal ions. The  $\gamma_{\text{HO}_2}$  is controlled by  $\text{HO}_2$  self-reaction in the aerosol particles and therefore decreases along the flow tube as  $[\text{HO}_2]_{\text{g}}$  decreases. High wall losses and high particle concentrations can cause  $\gamma_{\text{HO}_2}$  to decrease significantly as a function of reaction time, which should be acknowledged when analysing  $\text{HO}_2$  uptake measurement data in the future. This time dependence may increase with increasing RH, as wall losses and gas-phase reaction rate coefficients increase leading to lower  $\text{HO}_2$  concentrations along the flow tube.<sup>80</sup> To obtain accurate  $\gamma_{\text{HO}_2}$  values it is necessary to use a model which accounts for decreasing  $\text{HO}_2$  concentrations along the flow tube.

The value of  $\gamma_{\text{HO}_2}$  onto particles containing transition metal ions also has the potential to be time dependent in experiments if Fenton-like chemistry is occurring.  $\text{HO}_2$  reformation from  $\text{H}_2\text{O}_2$  would decrease the observed  $\gamma_{\text{HO}_2}$  as the  $\text{HO}_2 : \text{H}_2\text{O}_2$  ratio decreases along the flow tube. Further but challenging experiments in which  $\text{H}_2\text{O}_2$  concentrations are also measured would be required to confirm this. Gas-phase species such as  $\text{H}_2\text{O}_2$ , which partitions into aerosol particles in the aerosol flow tube and subsequently facilitates the formation of  $\text{HO}_2$ , have the capacity to elucidate variations observed in the scientific literature concerning diverse laboratory assessments of  $\gamma_{\text{HO}_2}$  onto Cu-doped particles. There may also be trace organic impurities in the gases or water used in the experiments which decompose in the presence of metal ions forming  $\text{HO}_2$ . Further investigations are required to determine whether any other species exist within the flow tube in addition to  $\text{H}_2\text{O}_2$ , that would form  $\text{HO}_2$  or  $\text{O}_2^-$  within the particle phase. For example, it is known that the trace  $\text{O}_2$  concentrations within the aerosol flow tube could react with trace iron and copper concentrations within the aerosol particles forming  $\text{O}_2^-$ .<sup>64,65</sup> Alternatively,  $\text{HO}_2$  radicals could be formed from other mechanisms; for example, trace levels of  $\text{O}_3$  reacting with  $\text{H}_2\text{O}_2$  can lead to the formation of radicals.<sup>81</sup> The presence of gas-phase species which reform  $\text{HO}_2$  in the atmosphere may lead to a decrease in the effective  $\gamma_{\text{HO}_2}$ . Further systematic measurements with known  $\text{H}_2\text{O}_2$  and transition metal ions will be required to better understand the impact of ambient  $\text{H}_2\text{O}_2$  concentrations in the atmosphere on the effective  $\gamma_{\text{HO}_2}$ .

The KM-SUB model was able to reproduce measurements of the  $\gamma_{\text{HO}_2}$  as a function of Cu relatively well with parameters consistent with previous work.<sup>31</sup> We speculate that the formation of  $\text{CuSO}_4$  may significantly reduce  $\gamma_{\text{HO}_2}$  in ammonium sulphate particles although this still needs to be further investigated. We demonstrate that increasing aerosol particle pH can significantly increase the uptake coefficient  $\gamma_{\text{HO}_2}$  of aerosol particles containing transition metal ions due to additional partitioning of  $\text{HO}_2$  into the particles and changes in the relative importance of different reactions. We have also demonstrated that although  $\gamma_{\text{HO}_2}$  will increase for larger particles, the effective uptake coefficient  $\gamma_{\text{HO}_2,\text{eff}}$ , which includes gas-phase diffusion limitations, will decrease significantly. This may lead to  $\gamma_{\text{HO}_2,\text{eff}}$ , which is the typical observable in experiments and parameter in atmospheric model simulations, being larger for smaller particles in the atmosphere.

It has been demonstrated that the value of  $\gamma_{\text{HO}_2}$  may vary significantly over the range of atmospherically relevant transition metal concentrations. This is consistent with previous measurements and modelling work.<sup>27,30–33,35,82</sup> Many factors may influence the value of  $\gamma_{\text{HO}_2}$  that should be used in atmospheric box models, such as the concentration of soluble transition metal ions, the particle composition, the pH, the aerosol particle size, and the presence of any compounds which reform  $\text{HO}_2$ . Other factors, such as bulk diffusion limitations or the presence of certain organics, can reduce  $\gamma_{\text{HO}_2}$ . As discussed in our previous work, an increase in aerosol particle viscosity can lead to a significant decrease in  $\gamma_{\text{HO}_2}$  for copper doped aerosol particles by decreasing the rate of diffusion of  $\text{HO}_2$  into the aerosol particles.<sup>54</sup> We have also previously observed a significant decrease in  $\gamma_{\text{HO}_2}$  from a value of the mass accommodation coefficient  $\alpha_{\text{HO}_2}$  to approximately two orders of magnitude less when oxalic acid is added to copper-doped aerosol particles.<sup>43</sup> In the current work we have not treated the interactions of Cu and Fe in aerosols, which may enhance  $\text{HO}_2$  uptake, prevent iron precipitation in ambient aerosols, and should be investigated in follow-up studies.<sup>63,83</sup> Transition metal distribution across all particles is usually assumed to be even by models. However, in reality, not all atmospheric particles contain transition metals that catalytically remove  $\text{HO}_2$  and enhance the value of  $\gamma_{\text{HO}_2}$ . This was discussed in a recent study in which Khaled *et al.*<sup>84</sup> hypothesise that  $\gamma_{\text{HO}_2}$  may be significantly lower for an atmospheric aerosol particle compared to an aerosol particle generated *via* atomisation in the laboratory using a bulk sample containing transition metal ions. Overall, additional experiments and modelling are required to fully understand the influence of different factors on the  $\text{HO}_2$  uptake coefficient.

## Conflicts of interest

There are no conflicts of interest to declare.

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