

Electronic Supplementary Information for:

## The Adsorption of Acetic Acid on Ice and its Co-adsorption with Nitrous Acid

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### Vapour pressure of solid acetic acid

Our experiment required low concentrations of acetic acid in a carrier gas at 1 atm. The acetic acid source therefore consisted of slowly passing the carrier gas over acetic acid at low temperatures (see below) assuming that the equilibrium vapour pressure of acetic acid is established. The gas phase concentration of CH<sub>3</sub>COOH in the experiments was then calculated using the temperature dependence of its vapour pressure. Given that this vapour pressure has not been fully measured in the past and that the published parameterizations result from a combination of experimental data and thermodynamic values (see below), we calibrated our experiments by measuring the vapour pressure under the conditions of our acetic acid source by using the set up presented in Fig. S1. The experiments were performed as follows. A small flow of N<sub>2</sub> (0.5–10 mL min<sup>-1</sup>, all the flows given are normalized to the standard conditions of temperature and pressure and were controlled by mass flow controllers if not stated otherwise) was blown over frozen acetic acid (glacial 100%, Merck) kept at a temperature ranging between 223 and 263 K. The small N<sub>2</sub> flow containing CH<sub>3</sub>COOH was further diluted with N<sub>2</sub> (400 mL min<sup>-1</sup>) and O<sub>2</sub> (100 mL min<sup>-1</sup>). The total flow (500.5–510.0 mL min<sup>-1</sup>) was then continuously injected in an oven kept at 800°C where CH<sub>3</sub>COOH was quantitatively oxidized to CO<sub>2</sub> on copper oxide (CuO). Carbon dioxide was measured directly after the oven by a calibrated commercial CO<sub>2</sub> analyser (Thermo Environmental Instruments Inc., MODEL 41C Trace Level). From the measured CO<sub>2</sub> concentration, the

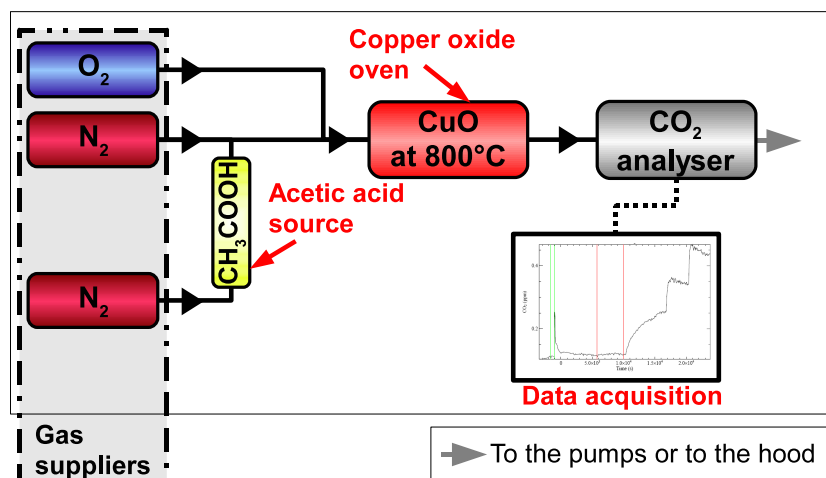


Figure S1: Schematic of the experimental set-up used to re-measure the vapour pressure of solid acetic acid. Flow directions are marked by arrows. Dashed lines represent electronic connections.

acetic acid vapour pressure in the source could be retrieved. The main difficulty is to consider dimerisation.

The equilibrium constant,  $K_{\text{eq}}$  of the dimerisation reaction,



has been reported by Chao and Zwolinski<sup>1</sup>, for temperatures ranging between 100 and 900 K. By fitting these data between 100 to 500 K, we obtained

$$\ln K_{\text{eq}}(T) = -(18.73 \pm 0.29) + \frac{(7742 \pm 57)}{T}, \quad (\text{S1})$$

where  $T$  [K] is the absolute temperature. Considering the chemical equation of dimerisation in the acetic acid source, one can write,

$$K_{\text{eq}}(T) = \frac{P_{\text{d,s}}}{(P_{\text{m,s}})^2} P_0, \quad (\text{S2})$$

where  $P_{\text{m,s}}$  [Pa] and  $P_{\text{d,s}}$  [Pa] are the pressures of monomers and dimers in the acetic acid source, respectively and  $P_0$  is the standard pressure which is equal to 101 325 Pa.

The relation between  $P_{\text{CO}_2}$  [Pa], the  $\text{CO}_2$  concentration measured at the exit of the oven and  $P_{\text{m}}$  and  $P_{\text{d}}$  [Pa] – the pressures of monomers and dimers in the gas flow entering the oven, respectively – can be written as

$$P_{\text{CO}_2} = 2P_{\text{m}} + 4P_{\text{d}}. \quad (\text{S3})$$

Khamaganov *et al.*<sup>2</sup> showed that the monomer/dimer concentration ratio in the source before dilution can be calculated from the *weighted* sum of acetic acid pressures,  $P_{\text{w}} = P_{\text{m}} + 2P_{\text{d}}$ . Knowing that  $2P_{\text{w}} = P_{\text{CO}_2}$ , it leads to

$$P_{\text{CO}_2} = 2(P_{\text{m},\text{s}} + 2P_{\text{d},\text{s}}) \frac{P_{\text{tot}}}{P_{\text{tot},\text{s}}} \frac{F_{\text{tot},\text{s}}}{F_{\text{tot}}}, \quad (\text{S4})$$

where  $P_{\text{tot},\text{s}}$ ,  $F_{\text{tot},\text{s}}$  and  $P_{\text{tot}}$ ,  $F_{\text{tot}}$  are the total pressure and the total gas flow in the source and in the oven, respectively.

The total vapour pressure of acetic acid  $P_{\text{tot},\text{aa},\text{s}}$  [Pa] in the source is finally given by,

$$P_{\text{tot},\text{aa},\text{s}} = P_{\text{m},\text{s}} + P_{\text{d},\text{s}}. \quad (\text{S5})$$

Combining Eq. (S2), Eq. (S3), Eq. (S4) and Eq. (S5) leads to a second order equation of the form  $a(P_{\text{tot},\text{aa},\text{s}})^2 + bP_{\text{tot},\text{aa},\text{s}} + c = 0$ , where  $a$ ,  $b$  and  $c$  depend on  $K_{\text{eq}}(T)$ ,  $P_0$ ,  $P_{\text{CO}_2}$ ,  $P_{\text{tot},\text{s}}$ ,  $P_{\text{tot}}$ ,  $F_{\text{tot},\text{s}}$  and  $F_{\text{tot}}$ . This equation can be solved for  $P_{\text{tot},\text{aa},\text{s}}$  and has only one physically relevant solution.

The vapour pressure of  $\text{CH}_3\text{COOH}$ ,  $P_{\text{tot},\text{aa},\text{s}}$  as calculated from the  $\text{CO}_2$  measurements is presented in Fig. S2. The scatter observed at each temperature is mainly due to the fact that for each temperature, the  $\text{N}_2$  gas flow rate through the source was varied to check the stability of the source and the maximum flow rate which still allow saturation of the carrier gas. Though scatter occurs, we did not observe a systematic variation of  $P_{\text{CO}_2}$  with the  $\text{N}_2$  gas flow. Also in Fig. S2, we compare our measurements with the data available in the literature. It has to be noted that the temperature dependence of the vapour pressure of solid acetic acid previously reported was calculated

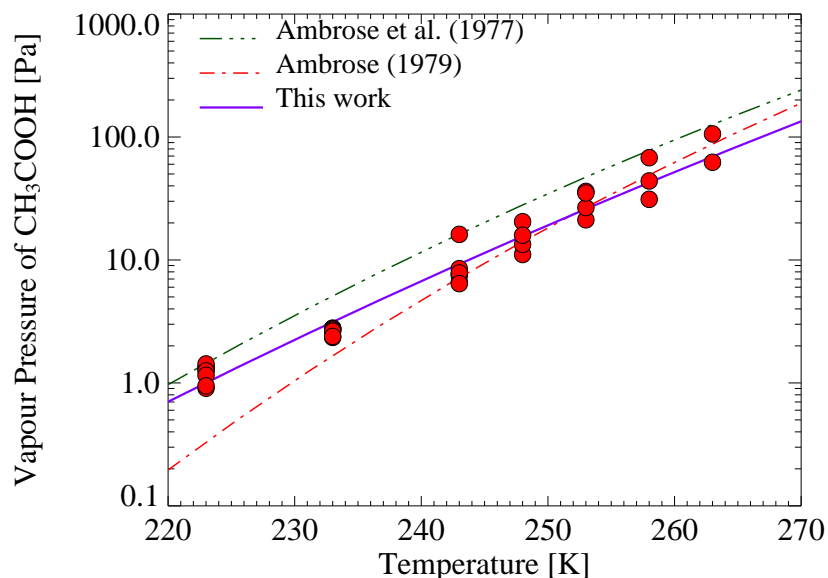


Figure S2: Vapour pressure of  $\text{CH}_3\text{COOH}$  as calculated from the  $\text{CO}_2$  measurements for different temperatures (red symbols) and its parameterization using Eq. (S6) (blue solid line). Dashed lines indicate literature values (see legend in the figure).

from the extrapolation of the vapour pressure of liquid acetic acid and the enthalpy of fusion<sup>3</sup> or from the sublimation enthalpy and some vapour pressure measurements at low temperature.<sup>4</sup> Moreover, Ambrose *et al.*<sup>3</sup> did not take into account dimerisation. Our measurements are grossly consistent with the calculated values, even though a slightly different temperature dependence is apparent. As the main purpose of this exercise was to obtain a calibration for our acetic acid source, we did not consider this difference further.

For convenience, the temperature dependence of the vapour pressure of acetic acid was parameterized using an Antoine's type equation of the form,

$$\log P_{\text{tot,aa,s}} = A - \frac{B}{T + C} \quad (\text{S6})$$

where  $P_{\text{tot,aa,s}}$  is expressed in bar and  $A = 14.45$ ,  $B = 7444$  and  $C = 159.8$ .

## Derivation of the monomer concentration

The monomer and dimer concentration of acetic acid in the gas mixture entering the packed ice bed was calculated from  $P_{\text{tot,aa,s}}$  as described above. The fraction of monomers is defined as  $x_{\text{m}} = P_{\text{m}}/(P_{\text{m}} + P_{\text{d}})$ .

## References

- [1] J. Chao and B. J. Zwolinski, *J. Phys. Chem. Ref. Data*, 1978, **7**, 363–377.
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