Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Gas-Chromatography using ice coated fused silica-columns: Study of adsorption of sulfur dioxide on water-ice" *by* Stefan Langenberg and Ulrich Schurath

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We thank the referee for reviewing and commenting our discussion paper. The remarks of the reviewer are marked like *this*. All references, symbols and equations used and cited herein refer to the discussion paper unless otherwise indicated. To the comments and questions we answer as follows:

Reply to general comments

We consider the manuscript worth to be published in ACP:

- A new gas chromatographic technique is presented to study trace gas – ice in-

teractions.

- A dissociative adsorption mechanism of SO_2 on ice limited to distinguished active sites is proposed. The mechanism should be validated in future by theoretical calculations.

Reply to specific comments and questions

- The gas-phase concentrations of SO_2 seem too high to me. Extrapolation from experiments at such high concentrations to environmental concentrations – what are typical concentrations of SO_2 in air masses in contact with ice or snow anyway, please specify in introduction – is highly questionable for a number of reasons as shown for a number of trace gases (see later work on HNO_3 by Abbatt group). This lets me question the environmental relevance of this work.

We agree that the high concentrations are a limitation of our study. Just our experiments show that trace gas ice interactions dramatically can change when changing the concentration range.

In the lower troposphere SO_2 concentrations < 50 ppbv (Heikes et al., 1987, http://dx.doi.org/10.1029/JD092iD01p00915) are found. This corresponds to $p(SO_2) < 0.005$ Pa which is at the lower concentration range of our study.

Our study was motivated by the assumption of vertical trace gas transport in the wake of an aircraft by adsorption and subsequent sedimentation. Higher SO_2 concentrations than in the troposphere were expected in the plume. However, later Schumann et al. (1998) showed that the plume is rapidly diluted with ambient air. Therefore, within few seconds, the SO_2 concentration drops to $5 \times 10^8 - 2 \times 10^{10}$ cm^{-3} which is about two decimal powers lower than the concentration range investigated. However, we could show that our measurements are consistent with the work of Clegg and Abbatt (2001) when extrapolating our model to lower concentrations.

Weak physisorption and dissociative adsorption at active sites are different processes and must be considered separately.

Regarding the physisorption of SO$_2$ at the normal ice surface: using Eq. (8) and $K_L = 1.35 \times 10^{-8}$ mol m^{-2}Pa^{-1}, only a surface coverage $\theta = 0.2\%$ is found at a peak partial pressure of $p(\text{SO}_2) = 1$ Pa. Thus, SO$_2$-SO$_2$ interactions can be neglected.

Regarding adsorption at the active sites: using Eq. (15) at 205 K the degree of saturation of the active sites is $\theta = 97\%$ and at 266 K $\theta = 87\%$.

Therefore, during the chromatographic experiments nearly complete saturation of the active sites but not of normal surface is achieved at peak maximum.

The existence of active sites responsible for dissociative adsorption is also surprising for us. The surface saturation capacity for dissociative adsorption is so low, because dissociative adsorption must be caused only by active sites, see discussion section in our paper.

For acetone, we did not find any evidence for adsorption at active sites. However, this is not surprising because acetone does not dissociate in aqueous solution. Tailing observed for the acetone peaks is caused by saturation of the normal ice surface.

Regarding the adsorption of acetone at the normal ice surface, our data are consistent with other studies published previously, see Fig. 6.

We assume that the referee refers to Crowley et al. (2010), a report of the IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry. Therein, the linear adsorption isotherm is defined as

$$K_{\text{linC}} = [\text{X}]_s/[\text{X}]_g.$$

with $[K_{\text{linC}}] = $ cm. K_{linC} and K_H can easily be converted by

$$K_{\text{linC}} = RTK_H.$$

Also therein, the Langmuir isotherm is defined as

$$\theta = \frac{K_{\text{LangC}}[\text{X}]_g}{1 + K_{\text{LangC}}[\text{X}]_g}$$

with $[K_{\text{LangC}}] = $ cm^3. K_{LangC} is related to K_L by

$$K_{\text{LangC}} = \frac{RTK_L}{q_s}.$$

The units are different and therefore, K_{linC} is not comparable with K_{LangC}. In the IUPAC report cm is used as base unit. This may facilitate the integration of the data into kinetic atmospheric models. Outside this application, using cm as base unit is error-prone, since unit conversions are required. Therefore, we formulated the adsorption isotherms purely with SI-units as function of partial pressure instead of particle density, what we do not intend to change. This has the advantage that adsorption enthalpies directly can be obtained from the van't Hoff plot.

that the freezing point depression by SO$_2$ is rather modest, I do not expect a large impact but clarification is needed.

This subject was already discussed by Huthwelker et al. (2001): Rather large SO$_2$ partial pressures higher than in our experiments are required to form aqueous SO$_2$ solutions or the SO$_2$·6H$_2$O hydrate. They also report the phase diagram of the system H$_2$O-SO$_2$.

To achieve melting of the ice surface by freezing point depression, a solute must be solved in the ice surface with a mole fraction

$$x_s > \frac{\Delta H_m \Delta T}{R T_m^2}$$

where $\Delta H_m = 6008\,\mathrm{J\,mol^{-1}}$ is the melting enthalpy of ice and T_m the melting temperature.

The partial pressure of the trace gas must exceed a certain threshold value to achieve melting of the ice surface. $x_s(\mathrm{SO_2})$ and $p(\mathrm{SO_2})$ are interconnected by Henry's law yielding

$$p(\mathrm{SO_2}) \approx \frac{x_s(\mathrm{SO_2})}{M(\mathrm{H_2O})H}$$

where $M(\mathrm{H_2O}) = 0.018\,\mathrm{kg\,mol^{-1}}$ and H is the Henry coefficient of SO$_2$ in supercooled water. The coefficient is obtained from data of water after extrapolating to lower temperatures, see Langenberg et al. (1998). Therefore, for the temperature limits of our experiment, the following values are obtained, assuming full dissociation of SO$_2$:

T [K]	ΔT [K]	$x_s(\mathrm{SO_2})$	H [mol kg bar^{-1}]	$p(\mathrm{SO_2})$ [Pa]
205	68	0.66	797	> 2300
265	8	0.08	4	$> 6 \times 10^4$

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Since the partial pressure of SO$_2$ in our experiment is much lower, surface melting by freezing point depression is not expected. However, the freezing point of ice may be depressed in veins and nodes. Huthwelker et al. (2001) postulated that slow uptake of SO$_2$ is caused by uptake in these liquid reservoirs. We also observed slow uptake, but we did not analyze it quantitatively.

The revised manuscript was not changed anymore, it is attached as supplement in final form with all changes applied.

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2017-800/acp-2017-800-AC2-supplement.pdf

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