

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

Anonymous Referee #1

Received and published: 3 January 2018

This is an excellent piece of scientific work that fills a gap owing to the chosen temperature range of 205 to 265 K, a range which most studies do not explore. In addition, it uses a simple experimental technique that is rarely used in the present context despite its widespread use in separation sciences. I highly appreciate the present work as it corresponds to a thorough and thoughtful experimental study including random error and uncertainty estimates as well as the confrontation of experimental data with three models of SO₂ surface interaction at increasing complexity. It always appeals to compare different methods of experimental techniques for a given problem of some importance in order to gauge the possible existence of measurement artifacts or fallacies as a confidence building principle. The present study undertakes exactly this which

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contributes to its importance and value.

At this point I would like to raise a few questions that the authors should try to answer during the peer-review process in order to help the reader grasp the full significance of the work:

- The slow and inexorable "Degradation" of the ice film owing to the carrier gas decompression (pg. 3, lines 19 and 20, and equation (1)) should be explained in a bit more detail. Is this a temperature effect owing to adiabatic decompression across the length of the capillary? If one has a flow with an equilibrium amount of humidity in the carrier gas one loses this same amount at the exit to first order: What goes in must come out at the end of the capillary. What you lose by sublimation is redeposited downstream, provided we are at steady-state and have a uniform temperature profile. What else is implied or important beyond that? Any unaccounted loss processes? Please explain the scientific basis or complications.

- I strongly suggest the addition of a qualitative explanation for the concentration dependence of the SO₂ retention time displayed in Figure 2. As far as I understand this effect it comes from the (partial) saturation of the SO₂ uptake (at equilibrium): The higher the SO₂ concentration the earlier the breakthrough because of vanishing interaction with the ice owing to surface saturation of the uptake following equation (11) (Langmuir dissociation, strong interaction) and (3) (Henry adsorption isotherm, weak interaction).

- The Temkin isotherm (equation (5)) seems to be a parametric treatment of the above behavior according to the derivation in the S1 section: Is there any scientifically rooted explanation to simply add algebraically both contributions (Henry + each of the stronger interactions) in all three models displayed in Table 1 as an "interpolation" or superposition scheme of two extremes? The molecular view (saturation to a variable degree depending on the SO₂ partial pressure) naturally arrives at the same result for purely kinetic reasons. Diffusion tube experiments under molecular flow conditions (T. Koch

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et al., JPCA 1998; C. Alcala-Jornod et al., PCCP 2000; C. Alcala-Jornod et al., JPCA 2004) arrived at the identical saturation behavior of salt and ice interfaces (without the presence of a carrier gas).

- What is the rationale for using "deactivated" (alkyl-silylated) Pyrex as a Substrate to grow the ice sample in the first place? I do not believe that a coating of several micrometers will let the SO₂ "feel" the underlying properties of the substrate. From our own studies of pure ice performing quartz crystal microbalance measurements on the evaporation rate of H₂O from pure ice films result in a value of 80 to 100 nm thick layer beyond which subsurface effects cease to be important. Beyond this thickness the kinetics of evaporation is unchanged up to several micrometer thickness of pure vapor-deposited ice which is believed to be less compact (lower density, more surface imperfections) than ice samples frozen from pure water. By the same token, an interference of the silylated glass interface with ice at several micrometers thickness is highly unlikely (pg. 13, lines 30 and 31, and pg. 15, lines 15 and 16) unless the authors have solid evidence to the contrary.

- Regarding the strongly tailing peak shapes of the chromatograms for SO₂, and to a lesser extent for acetone: Is this a thermodynamic or kinetic effect? Is the equilibrium between adsorbed and gas phase SO₂ established at low concentrations of SO₂ at constant flow rate?

- As a general remark the units of KH, KL and q should be clearly included, at least once when mentioned in the text for the first time. One has to be aware that Henry's adsorption isotherm (KH) is different from Henry's law solubility constant (gas-bulk partition coefficient)!

In addition, there are several minor technical points that may be raised:

- Regarding the square root dependence of the surface coverage (equation (15) and pg. 8, line 16) the requirement is that the active sites must be NEIGHBORING sites in order to yield the square root dependence. - Pg. 2, line 30 and 31: sentence does

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not make sense! - Pg. 3, line 20: "...ice film slowly but unavoidably..." - Pg. 4, lines 15 and 16: Incomplete sentence. - Pg. 8, line 5: I do not see a temperature effect in Figure 2b. It probably must be Figure 3b. - Pg. 7, Figure 3: I do not see yellow data points, however there is a yellow (fitted) line. - Pg. 10, bottom: "miscible". - Pg. 12, Table 2: units of KH: mol m⁻²Pa⁻¹.

Please also note the supplement to this comment:

<https://www.atmos-chem-phys-discuss.net/acp-2017-800/acp-2017-800-RC1-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2017-800>, 2017.

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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

Stefan Langenberg and Ulrich Schurath

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Received and published: 16 January 2018

We thank the referee for reviewing and commenting our discussion paper. The remarks of the reviewer are marked like *this*. To the comments and questions we answer as follows:

Reply to specific comments and questions

- The slow and inexorable “Degradation” of the ice film owing to the carrier gas decompression (pg. 3, lines 19 and 20, and equation (1)) should be explained in a bit more detail. Is this a temperature effect owing to adiabatic decompression across the length

C1

of the capillary? If one has a flow with an equilibrium amount of humidity in the carrier gas one loses this same amount at the exit to first order: What goes must come out at the end of the capillary. What you lose by sublimation is redeposited downstream, provided we are at steady-state and have a uniform temperature profile. What else is implied or important beyond that? Any unaccounted loss processes? Please explain the scientific basis or complications.

The flow through the column is described by Poiseuille’s equation for compressible fluids. It is assumed that the temperature of the carrier is permitted to equilibrate with the column wall. Due to the decompression of the carrier gas along the column at constant temperature, the mixing water vapor in equilibrium with the ice surface increases along the flow tube. Therefore, while the mass flow rate of the carrier gas \dot{n} is constant, the mass flow rate of water vapor increases along the ice-coated column.

It is assumed that the water vapor pressure $p(\text{H}_2\text{O})$ is in equilibrium with the ice surface. The mass flow of water leaving the column is given by

$$\dot{n}_o(\text{H}_2\text{O}) = \frac{p(\text{H}_2\text{O})\dot{V}_o}{RT}$$

where \dot{V}_o is the volume flow rate of the carrier gas at column exit. It is calculated from the carrier gas mass flow rate \dot{n} and the carrier gas pressure at column exit p_o :

$$\dot{V}_o = \frac{\dot{n}RT}{p_o}$$

Since the carrier gas entering the column is pre-humidified, the water mass flow entering the column is given by

$$\dot{n}_i(\text{H}_2\text{O}) = \frac{p(\text{H}_2\text{O})\dot{V}_i}{RT}$$

Due to carrier gas decompression $\dot{V}_i < \dot{V}_o$. Therefore, less water is entering the column

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than leaving. Hence, the net rate of water leaving the column is given by

$$\dot{n}(\text{H}_2\text{O}) = \dot{n}_o(\text{H}_2\text{O}) - \dot{n}_i(\text{H}_2\text{O}) = \dot{n}_p(\text{H}_2\text{O}) \left(\frac{1}{p_o} - \frac{1}{p_i} \right).$$

After calculating \dot{h} from $\dot{n}(\text{H}_2\text{O})$, Eq. (2) is obtained.

We conclude that our adsorption experiments were performed under desublimation conditions with respect to H_2O .

- I strongly suggest the addition of a qualitative explanation for the concentration dependence of the SO_2 retention time displayed in Figure 2. As far as I understand this effect it comes from the (partial) saturation of the SO_2 uptake (at equilibrium): The higher the SO_2 concentration the earlier the breakthrough because of vanishing interaction with the ice owing to surface saturation of the uptake following equation (11) (Langmuir dissociation, strong interaction) and (3) (Henry isotherm, weak interaction).

An explanation has been added to the introduction (p3, l5).

- The Temkin isotherm (equation (5)) seems to be a parametric treatment of the above behavior according to the derivation in the S1 section: Is there any scientifically rooted explanation to simply add algebraically both contributions (Henry + each of the stronger interactions) in all three models displayed in Table 1 as an "interpolation" or superposition scheme of two extremes? The molecular view (saturation to a variable degree depending on the SO_2 partial pressure) naturally arrives at the same result for purely kinetic reasons. Diffusion tube experiments under molecular flow conditions (T. Koch et al., JPCA 1998; C. Alcalá-Jornod et al., PCCP 2000; C. Alcalá-Jornod et al., JPCA 2004) arrived at the identical saturation behavior of salt and ice interfaces (without the presence of a carrier gas).

As we describe, the modified Temkin and Langmuir isotherms pass over to Henry's law of adsorption at very low concentration. But this type of adsorption must be a stronger chemisorption like adsorption process in contrast to the weaker physisorp-

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tion process. Both adsorption processes occur in parallel over the whole concentration range. Therefore, at very low concentration, the effective Henry's adsorption isotherm constant would be $K_H + K_T$. Even in case of dissociative adsorption, a linear adsorption behavior would be expected when $q(\text{H}_3\text{O}^+) > q(\text{HSO}_3^-)$.

- What is the rationale for using "deactivated" (alkyl-silylated) Pyrex as a Substrate to grow the ice sample in the first place? I do not believe that a coating of several micrometers will let the SO_2 "feel" the underlying properties of the substrate. From our own studies of pure ice performing quartz crystal microbalance measurements on the evaporation rate of H_2O from pure ice films result in a value of 80 to 100 nm thick layer beyond which subsurface effects cease to be important. Beyond this thickness the kinetics of evaporation is unchanged up to several micrometer thickness of pure vapor-deposited ice which is believed to be less compact (lower density, more surface imperfections) than ice samples frozen from pure water. By the same token, an interference of the silylated glass interface with ice at several micrometers thickness is highly unlikely (pg. 13, lines 30 and 31, and pg. 15, lines 15 and 16) unless the authors have solid evidence to the contrary.

Due to experimental constraints, about 1 m of the column inside the box remained uncoated. In order to minimize interfering adsorption of SO_2 on the ice-free surface, we used a methylsilyl-deactivated column. This is explained in the revised manuscript (p4, l18). We agree that SO_2 adsorption on the ice coating is not likely to be affected by the properties of the underlying tube surface. It is more likely that certain ice film properties e.g. surface roughness depend on the substrate. Unfortunately the microphysical properties of the ice coatings in our capillary columns could not be probed by our experimental techniques.

- Regarding the strongly tailing peak shapes of the chromatograms for SO_2 , and to a lesser extent for acetone: Is this a thermodynamic or kinetic effect? Is the equilibrium between adsorbed and gas phase SO_2 established at low concentrations of SO_2 at constant flow rate?

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The most likely cause of the tailing is nonlinear adsorption at low temperature. This is supported by the decreasing adjusted retention times t_n with increasing amounts of acetone injected. Therefore, Eq. (18) was used to extrapolate our measurements to zero concentration. However, we cannot exclude additional tailing due to slow incorporation of acetone into the ice surface even at higher temperatures. We assume that adsorption equilibrium of SO_2 on ice is established with respect to physisorption and dissociative adsorption but not with respect to uptake into the ice surface under our experimental conditions.

- As a general remark the units of K_H , K_L and q should be clearly included, at least once when mentioned in the text for the first time. One has to be aware that Henry's adsorption isotherm (K_H) is different from Henry's law solubility constant (gas-bulk partition coefficient)!

K_H , K_T and K_L have the same unit. This makes them comparable between themselves. After first occurrence of the symbols in the text, the unit has been denoted now in the revised manuscript.

The term *Henry's law of adsorption* was adopted from Wikipedia, see https://en.wikipedia.org/wiki/Henry_adsorption_constant: "The Henry adsorption constant is the constant appearing in the linear adsorption isotherm, which formally resembles Henry's law; therefore, it is also called Henry's adsorption isotherm."

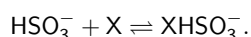
- Regarding the square root dependence of the surface coverage (equation (15) and pg. 8, line 16) the requirement is that the active sites must be NEIGHBORING sites in order to yield the square root dependence.

This is required for the steady state derivation of Eq. (15) given by Huthwelker et. al (2006). However, Eq. (15) is a thermodynamic relation. It can also be derived as follows on a pure thermodynamic base:

We assume that HSO_3^- is trapped by an unknown ice surface defect X. In addition to

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equilibrium (R1) there is a second equilibrium



The total surface concentration of X is limited to q_S . This equilibrium corresponds to Langmuir adsorption of HSO_3^- on ice.

Reply to proposed technical corrections

- Pg. 2, line 30 and 31: sentence does not make sense!

Fixed.

- Pg. 3, line 20: "...ice film slowly but unavoidably..."

Fixed.

- Pg. 4, lines 15 and 16: Incomplete sentence.

Fixed.

- Pg. 8, line 5: I do not see a temperature effect in Figure 2b. It probably must be Figure 3b.

Fixed.

- Pg. 7, Figure 3: I do not see yellow data points, however there is a yellow (fitted) line.

Due to a strange software error, some points were not colored correctly. A workaround has been applied. A color palette better suited for printout has been chosen.

- Pg. 10, bottom: "miscible".

Fixed.

- Pg. 12, Table 2: units of K_H : $\text{mol m}^{-2} \text{Pa}^{-1}$.

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$\ln K_H$ must be dimensionless, therefore K_H must be divided by $1 \text{ mol m}^{-2} \text{ Pa}^{-1}$. To clarify this, two braces have been added.

The revised marked-up version of the discussion paper is attached as supplement.

Please also note the supplement to this comment:

<https://www.atmos-chem-phys-discuss.net/acp-2017-800/acp-2017-800-AC1-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2017-800>, 2017.

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

Anonymous Referee #3

Received and published: 21 February 2018

The study presents results from solid-gas chromatography of several trace gases to ice. The work covers a T range of 205 to 265 ÅK. From these, conclusions about the partitioning of SO₂ to ice in the upper troposphere and of the role of surface disorder on the partitioning are drawn. The partitioning of SO₂ to ice has raised quite a discussion in the community and is far from being understood. Further, the role of surface disorder is a key-topic. This makes the topic of the manuscript highly relevant for ACP.

I'm not convinced that this manuscript presents new and innovative results and fear the technical content is addressing only a very small and specific part of the atmospheric science community. I also find it difficult to capture the results based on the

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data presented. While I acknowledge the re-analysis and am enthusiastic about process modelling to derive fundamental data from chromatographic results, I'm sorry to suggest rejecting this manuscript.

* The gas-phase concentrations of SO₂ seem too high to me. Extrapolation from experiments at such high concentrations to environmental concentrations – what are typical concentrations of SO₂ 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 HNO₃ by Abbatt group). This lets me question the environmental relevance of this work. * The high concentrations obviously results in very high formal surface coverages, so that SO₂-SO₂ interactions can not be excluded. I don't understand the use of the Henry or Langmuir parameterization in this context – which strictly speaking works best at low coverage. What is the surface coverage at the peak position in your columns? * I don't understand why your surface saturation capacity is so low? To me this looks like there is something odd with the analysis. Could you convince me with the acetone data that your approach is working? * May I ask you to stick to the IUPAC nomenclature. So, your Henry would become K_{LinC}, for example. * Working with SO₂ and in acknowledgement of Huthwelkers work highlighting the role of solvation into liquid pockets, I strongly suggest to discuss the phase diagram. Taken that the freezing point depression by SO₂ is rather modest, I do not expect a large impact but clarification is needed.

Last, the manuscript remains very technical without a clear discussion on what is to be learned from fitting the chromatographic results.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-800, 2017.

C2

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

Stefan Langenberg and Ulrich Schurath

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Received and published: 25 February 2018

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-
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teractions.

- A dissociative adsorption mechanism of SO₂ 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 SO₂ seem too high to me. Extrapolation from experiments at such high concentrations to environmental concentrations – what are typical concentrations of SO₂ 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 HNO₃ 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 SO₂ concentrations < 50 ppbv (Heikes et al., 1987, <http://dx.doi.org/10.1029/JD092iD01p00915>) are found. This corresponds to $p(\text{SO}_2) < 0.005 \text{ Pa}$ 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 SO₂ 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 SO₂ concentration drops to $5 \times 10^8 - 2 \times 10^{10} \text{ cm}^{-3}$ 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.

- The high concentrations obviously results in very high formal surface coverages, so that SO₂-SO₂ interactions can not be excluded. I don't understand the use of the Henry or Langmuir parameterization in this context – which strictly speaking works best at low coverage. What is the surface coverage at the peak position in your columns?

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

Regarding the physisorption of SO₂ at the normal ice surface: using Eq. (8) and $K_L = 1.35 \times 10^{-8} \text{ mol m}^{-2} \text{ Pa}^{-1}$, only a surface coverage $\theta = 0.2\%$ is found at a peak partial pressure of $p(\text{SO}_2) = 1 \text{ Pa}$. Thus, SO₂-SO₂ 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.

- I don't understand why your surface saturation capacity is so low? To me this looks like there is something odd with the analysis. Could you convince me with the acetone data that your approach is working?

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.

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- May I ask you to stick to the IUPAC nomenclature. So, your Henry would become K_{LinC} , for example.

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 $[K_{\text{linC}}] = \text{cm}$. 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 $[K_{\text{LangC}}] = \text{cm}^3$. 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.

- Working with SO₂ and in acknowledgment of Huthwelkers work highlighting the role of solvation into liquid pockets, I strongly suggest to discuss the phase diagram. Taken

C4

that the freezing point depression by SO₂ 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 SO₂ partial pressures higher than in our experiments are required to form aqueous SO₂ solutions or the SO₂·6H₂O hydrate. They also report the phase diagram of the system H₂O-SO₂.

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

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

where $\Delta H_m = 6008 \text{ J mol}^{-1}$ 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. $x_s(\text{SO}_2)$ and $p(\text{SO}_2)$ are interconnected by Henry's law yielding

$$p(\text{SO}_2) \approx \frac{x_s(\text{SO}_2)}{M(\text{H}_2\text{O})H}$$

where $M(\text{H}_2\text{O}) = 0.018 \text{ kg mol}^{-1}$ and H is the Henry coefficient of SO₂ 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 SO₂:

T [K]	ΔT [K]	$x_s(\text{SO}_2)$	H [mol kg bar ⁻¹]	$p(\text{SO}_2)$ [Pa]
205	68	0.66	797	> 2300
265	8	0.08	4	> 6×10^4

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Since the partial pressure of SO₂ 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 SO₂ 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>

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2017-800>, 2017.

C6

Gas-Chromatography using ice coated fused silica-columns: Study of adsorption of sulfur dioxide on water-ice

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Abstract. The well-established technique of gas chromatography is used to investigate interactions of sulfur dioxide with a crystalline ice film in a fused silica wide-bore column. Peak shape analysis of SO₂ chromatograms measured in the temperature range 205 – 265 K is applied to extract parameters describing a combination of three processes: (i) physisorption of SO₂ at the surface; (ii) dissociative reaction with water; (iii) slow uptake into bulk ice. Process (ii) is described by a dissociative Langmuir isotherm. The pertinent monolayer saturation capacity is found to increase with temperature. The impact of process (iii) on SO₂ peak retention time is found to be negligible under our experimental conditions.

By analyzing binary chromatograms of hydrophobic ~~n-hexane~~ n-hexane and hydrophilic acetone, the premelt surface layer is probed in the temperature range 221 – 263 K possibly giving rise to irregular adsorption. Both temperature dependencies fit simple van't Hoff equations as expected for process (i), implying that irregular adsorption of acetone is negligible in the probed temperature range. Adsorption enthalpies of -45 ± 5 kJ mol⁻¹ and -23 ± 2 kJ mol⁻¹ are obtained for acetone and n-hexane.

Our study was motivated to assess the vertical displacement of SO₂ and acetone in the wake of aircraft by adsorption on ice particles and their subsequent sedimentation. Our results suggest that this transport mechanism is negligible.

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1 Introduction

Adsorption of SO₂ on ice surfaces is of interest in the chemistry and physics of the troposphere and stratosphere. In particular, large ice particles in contrails have been shown by LIDAR soundings to settle out fairly rapidly (Schumann, 1994). This gave rise to speculations that sedimentation of ice particles provides a significant mechanism for the vertical displacement of SO₂ and possibly other adsorbing trace gases, particularly in the upper troposphere. An analogous mechanism has been addressed for the absorption and desorption of SO₂ in raindrops falling through the plume of a power station (Walcek and Pruppacher, 1983). Therefore, Langenberg (1997) investigated the adsorption of the water-soluble aircraft exhaust ingredients SO₂ and acetone on ice over a wide temperature range. The data were interpreted in terms of a simple Langmuir model: SO₂ is weakly adsorbed at the normal ice surface and much more strongly at active surface sites. Huthwelker et al. (2006) and Crowley

et al. (2010) found that the results of Langenberg were in disagreement with the work Clegg and Abbatt (2001) and other investigators: in contrast to these studies, Langenberg's analysis implied a classical temperature dependence, i.e. more SO₂ being adsorbed at lower temperatures. In addition, the surface coverage derived from the data of Langenberg (1997) is about an order of magnitude lower than implied by the data of Clegg and Abbatt (2001). Therefore, we have reanalyzed the experiments of Langenberg (1997) using more sophisticated linear and nonlinear regression techniques using R (R Core Team, 2016). The experimental results and their reanalysis are published in the peer-reviewed literature for the first time.

The interaction of SO₂ with ice can be separated into fast and much slower components, as summarized by Huthwelker et al. (2006), Abbatt (2003) and Crowley et al. (2010). In the works of Chu et al. (2000) and Clegg and Abbatt (2001) the fast interaction was probed. Both used low pressure flow tubes interfaced with a mass spectrometer to measure SO₂. The former studied vapor-deposited ice coatings, while the latter used ice that was prepared by freezing a liquid water film. The experiments of Chu et al. (2000) were performed under non-equilibrium conditions on a time scale < 10 ms, revealing an initial uptake coefficient of $\gamma = 10^{-5}$ for SO₂ at 191 K.

Clegg and Abbatt (2001) measured adsorption / desorption bursts of SO₂ on ice in the range 213 – 238 K using SO₂ partial pressures between 10⁻⁵ – 10⁻³ Pa in helium. They could show that the equilibrium amount of SO₂ adsorbed on ice scaled with the square root of its partial pressure above the surface. They concluded that the square root dependence results from fast dissociative adsorption of SO₂ at the ice surface:



Experiments on orders of magnitude longer time scales utilizing packed ice columns in the temperature range 213 – 270 K (Clapsaddle and Lamb, 1989; Sommerfeld and Lamb, 1986; Conklin et al., 1993; Conklin and Bales, 1993) have revealed that SO₂ is eventually incorporated in ice and partially oxidized to H₂SO₄. The uptake rate increases with temperature and with a less than linear dependence on the SO₂ partial pressure. The experimental data were reanalyzed and interpreted by Huthwelker et al. (2001) in terms of SO₂ diffusing into an internal reservoir. For various reasons the packed column experiments were not suitable to study fast reversible adsorption on ice.

A long-standing issue in studies of gas-ice surface interactions is the possible involvement of a premelt layer (Bartels-Rausch et al., 2014). It is now well established that an extended quasi-liquid layer exists at the surface of pure water ice at temperatures of a few K below the melting point (Dash et al., 2006).

We employed a chromatographic technique to study adsorption of SO₂: ice was deposited as the stationary phase as a thin film of 2 – 8 μm thickness in a fused silica wide bore column (diameter $2r = 530 \mu\text{m} \pm 10\%$, length 10 m). Adsorption on the ice surface was studied by injecting small amounts of the trace gas under study spiked with a non-adsorbing tracer into the column. Due to adsorption, the trace gas was retained the *adjusted retention time* t_n relative to the non-adsorbing tracer ~~and therefore~~. Therefore, the inert tracer and the trace gas under study were separated and two peaks appear at the column outlet, where they were detected by a suitable detector. t_n was obtained from the peak maxima.

The slope of the adsorption isotherm was determined by the *peak maxima method* of gas-chromatography (Huber and Gerritse, 1971): from t_n and the column void time t_0 , the capacity ratio k' was measured as function of partial pressure p of

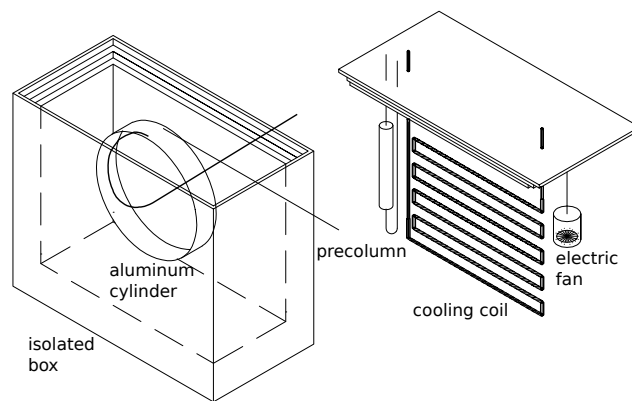


Figure 1. Exploded view of the box used for the coating procedure. Inside the box the air is recirculated by a fan (Micronel) to avoid temperature gradients. The temperature is monitored with two Pt-100 sensors mounted at the top and bottom of the box.

the trace gas under investigation. When using a capillary column with cylindrical geometry, k' is related to the slope of the isotherm by

$$k' = \frac{t_n}{t_0} = \left(\frac{\partial n_{ad}}{\partial n_g} \right) = \frac{2RT}{r} \left(\frac{\partial q}{\partial p} \right). \quad (1)$$

t_0 is calculated from the column dimensions, the carrier gas mass flow rate and the column head pressure, see e.g. (Langenberg et al., 1998; Giddings, 1991). It follows from Eq. (1) that if the isotherm is convex (like the Langmuir adsorption isotherm), the slope of which is continuously decreasing with increasing concentration, segments of the peak with high concentrations are moving faster through the column than at low concentrations. Therefore, the resulting chromatographic peak is tailing.

2 Experimental

Langenberg and Schurath (1999) described the coating procedure already in detail: a constant volume flow of air ($p = 1 - 2$ bar) was bubbled through a water reservoir at room temperature and admitted into the column maintained at 205 – 220 K. At the same time the column was slowly drawn through a pinhole into a cold box by a rotating aluminum drum inside the box which was driven by a stepping motor, see Fig. 1. The box was cooled by a recirculating thermostat (Lauda RLS 6) with a useful temperature range $T \geq 205$ K regulated to ± 1 K. The end of the fused silica column which was fixed to the aluminum drum was connected to a Teflon tube which was led out of the box through the axis of the aluminum cylinder. By slowly drawing the column into the cold box, the water vapor condensed and froze. In this way ice films of 2 - 8 μm thickness and ca. 8 m length could be prepared.

After finishing the coating procedure, the ice coated column was operated like an ordinary GC column with synthetic air as carrier gas. The flow rate was varied by means of a flow controller (ASM 10 – 100 sccm) while the column head pressure was monitored with a pressure transducer. The carrier gas from the flow controller was humidified using a precolumn filled with water saturated silica gel that was mounted inside the same cold box.

Although the carrier gas was humidified to match the vapor pressure over ice inside the cold box, the ice film slowly by-but unavoidably is degraded by sublimation due to carrier gas decompression along the length of the column. Since the carrier gas was pre-humidified to 100% relative humidity with respect to ice at each experimental temperature, the net evaporation rate from the ice surface is zero at the column head, but increases along the column. The rate of ice film thickness degradation \dot{h} is

5 given by

$$\dot{h} = \frac{V_m \dot{n} p(\text{H}_2\text{O})}{2\pi r l} \left(\frac{1}{p_o} - \frac{1}{p_i} \right), \quad (2)$$

where p_i is the column head pressure, p_o is the pressure at column exit, l is the length of the coated part of the column, \dot{n} the carrier gas mass flow and $V_m = 2 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ the molar volume of water-ice. At 265 K, $p_i = 2 \text{ bar}$, $p_o = 1 \text{ bar}$, $\dot{n} = 7.85 \times 10^{-5} \text{ mol s}^{-1}$ ($\approx 100 \text{ sccm}$) is $\dot{h} = 0.7 \mu\text{m h}^{-1}$. Vapor pressure $p(\text{H}_2\text{O})$ over ice is taken from Wexler (1977).

10 Some experiments were carried out using aged ice-films: after column preparation, the carrier gas was interrupted and the column was kept overnight at 265 K.

Void fused silica columns (SGE) are commercially available either with a pristine silica surface or with a methylsilyl-deactivated surface. Pristine silica surfaces are less hydrophobic than methylsilyl-deactivated silica surfaces. Wetting of the two column types was investigated by contact angle measurements using the capillary rise method (Bartle et al., 1981; Ogden and

15 McNair, 1986). For non wettable surfaces, the contact angle is $\vartheta > 90^\circ$ and for wettable surfaces is $\vartheta < 90^\circ$. For the untreated column $\vartheta = 63 \pm 1^\circ$ and for the methylsilyl-deactivated column $\vartheta = 111 \pm 1^\circ$ was found. To remove ionic impurities, the columns were rinsed with Milli-Q water prior to each coating procedure. The experiments were performed using methylsilyl-deactivated columns unless otherwise indicated. We expected that using the methylsilyl-deactivated columns, interactions of the trace gas with the uncoated part of the column could be minimized.

20 dependent chromatograms at 2 or 3 constant temperatures were recorded. The temperature was increased in steps of about 15 K ~~→~~ keeping the column for 1 h at each new temperature to achieve thermal equilibrium. In our studies of SO_2 adsorption the peak partial pressure was in the range $p = 0.001 - 1 \text{ Pa}$ at column exit.

10 – 500 μl dilute mixtures of the compound under study and an appropriate inert tracer were injected with a gas tight syringe. For mixtures of SO_2 and SF_6 a modified Bendix flame photometric sulfur monitor (Farwell and Barinaga, 1986)

25 was used, where SF_6 was the non adsorbable tracer. Acetone, *n*-hexane and methane were monitored using a Carlo Erba flame ionization detector. Here methane was used as non adsorbable tracer. The detector signal was amplified by a Keithley microvoltmeter and recorded by computer.

Due to experimental constraints, about 1 m of the column inside the box remained uncoated. In order to exclude artifacts from this ice-free section the adsorption of SO_2 in a totally ice free column was also investigated. The obtained k' values

30 ranged from 0.35 – 0.45 at 219 K and 0.15 – 0.25 at 234 K. At $T > 248 \text{ K}$ SO_2 and SF_6 could no longer be separated. Thus, interference by 1 m ice free column may be neglected for the lower concentration range of the isotherm.

Table 1. Nonlinear fit of the experimental data with humidified carrier gas and $h > 4 \mu\text{m}$ to different models. The binary variable ν denotes if the column was aged ($\nu = 1$) or not ($\nu = 0$).

Model	Model Parameters	P	Residual standard error
Temkin + Henry Eq. (7)	$\zeta = (a_1 + a_2T)(1 + a_3\nu)$		0.1977
	$a_1 = -(9 \pm 1) \times 10^{-9} \text{ mol m}^{-2}$	< 0.01	
	$a_2 = (4.8 \pm 0.5) \times 10^{-11} \text{ mol m}^{-2}\text{K}^{-1}$	< 0.01	
	$a_3 = 0.6 \pm 0.2$	< 0.01	
	$K_H = (1.11 \pm 0.08) \times 10^{-8} \text{ mol m}^{-2}\text{Pa}^{-1}$	< 0.01	
Langmuir + Henry Eq. (10)	$K_L = a_1 \exp(a_2/T)$		0.2066
	$q_S = a_3(1 + a_4\nu)$		
	$a_1 = (9 \pm 13) \times 10^{-16} \text{ mol m}^{-2}\text{Pa}^{-1}$	0.49	
	$a_2 = (5 \pm 0.4) \times 10^3 \text{ K}$	< 0.01	
	$a_3 = (1.10 \pm 0.08) \times 10^{-8} \text{ mol m}^{-2}$	< 0.01	
	$a_4 = 0.9 \pm 0.2$	< 0.01	
	$K_H = (1.60 \pm 0.08) \times 10^{-8} \text{ mol m}^{-2}\text{Pa}^{-1}$	< 0.01	
Langmuir (Dissociation) + Henry Eq. (16)	$q_S = a_1 \exp(a_2/T)(1 + a_3\nu)$		0.1938
	$a_1 = (5 \pm 3) \times 10^{-6} \text{ mol m}^{-2}$	0.02	
	$a_2 = -(1.3 \pm 0.1) \times 10^3 \text{ K}$	< 0.01	
	$a_3 = 0.6 \pm 0.2$	< 0.01	
	$K_{I1}K_H = (7 \pm 5) \times 10^{-14} \text{ mol}^2 \text{ m}^{-4} \text{ Pa}^{-1}$	0.1	
	$K_H = (1.35 \pm 0.01) \times 10^{-8} \text{ mol m}^{-2}\text{Pa}^{-1}$	< 0.01	

3 Results

3.1 Adsorption of SO_2

For low concentrations the retention times of SO_2 are strongly dependent on the amount of SO_2 injected. The peaks exhibit strong tailing even at low $p(\text{SO}_2)$, see Fig. 2a.

- 5 For further analysis, the *peak maximum method* (Huber and Gerritse, 1971) is applied to determine $(\partial q/\partial p)$ as function of p : it is assumed that Eq. (1) applies to the peak maximum, an assumption which is verified afterwards by peak shape calculation, see discussion.

The most simplistic model for adsorption is Henry's adsorption isotherm: the surface concentration q as function of the gas partial pressure p is given by

$$10 \quad q = K_H p, \quad (3)$$

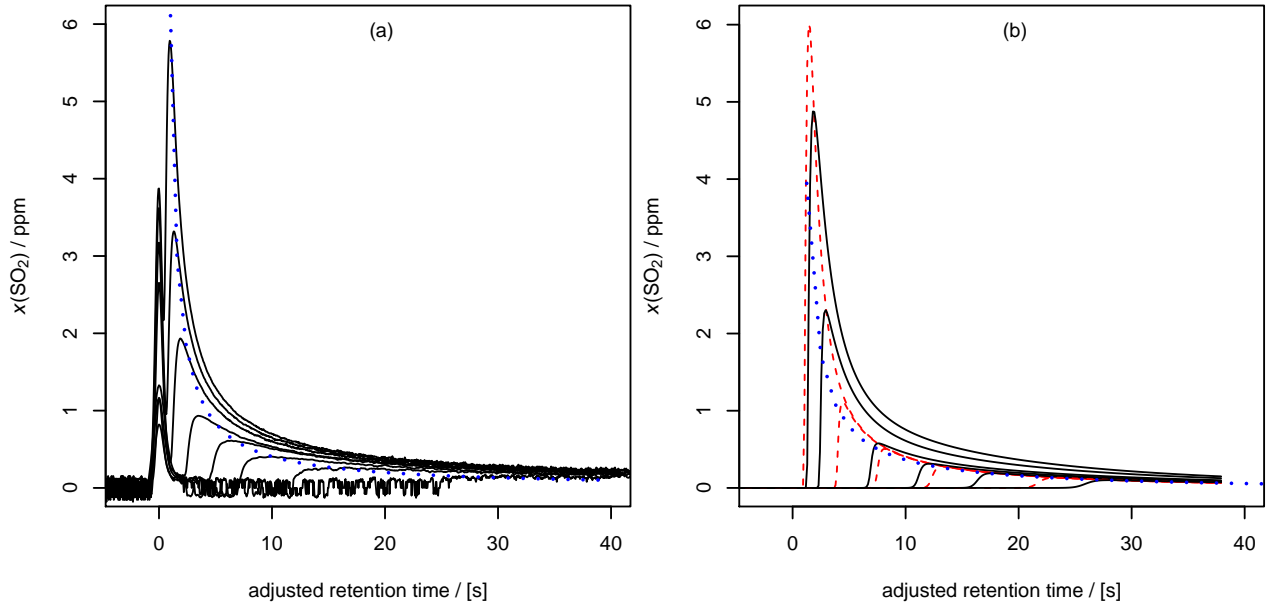


Figure 2. (a) Chromatograms from injection of various amounts of a SF_6/SO_2 mixture at 247 K and $2 \mu\text{m}$ ice film thickness. (b) Simulated SO_2 chromatograms using the Temkin isotherm with $\zeta = 4.3 \times 10^{-9} \text{ mol m}^{-2}$, $K_T = 10^{-6} \text{ mol m}^{-2}\text{Pa}^{-1}$, $K_H = 2.8 \times 10^{-9} \text{ mol m}^{-2}\text{Pa}^{-1}$ using 100 cells in axial direction. Dashed lines: simulation without absorption/diffusion into the solid phase. Solid lines: simulation including diffusion into the solid phase with $H = 50$, $D_s = 2 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ using 30 cells in radial direction. The dotted lines are calculated with Eq. (1). They represent the locations of the experimental peak maxima.

($[K_H] \equiv \text{mol m}^{-2} \text{ Pa}^{-1}$). After applying Eq. (1), we arrive at

$$k' = \frac{2RT}{r} K_H. \quad (4)$$

If adsorption of a compound is properly described by Henry's adsorption isotherm, the adjusted retention times should be independent of $p(\text{SO}_2)$ and thus, of the amount of adsorbing gas injected in our experiments. This is obviously only the case for high $p(\text{SO}_2)$. For lower $p(\text{SO}_2)$ an additional stronger adsorption mechanism comes into play which yields a $k' \propto p^{-1}$ dependency in the limit $p(\text{SO}_2) \rightarrow 0$.

An isotherm explaining such a partial pressure dependence is the Temkin-isotherm

$$q = \zeta \ln \left(\frac{K_T p}{\zeta} \right), \quad (5)$$

($[K_T] \equiv \text{mol m}^{-2} \text{ Pa}^{-1}$) see the supplement S1. Inserting the derivative of Eq. (5) in Eq. (1) yields the prevailing pressure dependence in the limit $p \rightarrow 0$

$$k' = \frac{2RT}{r} \frac{\zeta}{p}. \quad (6)$$

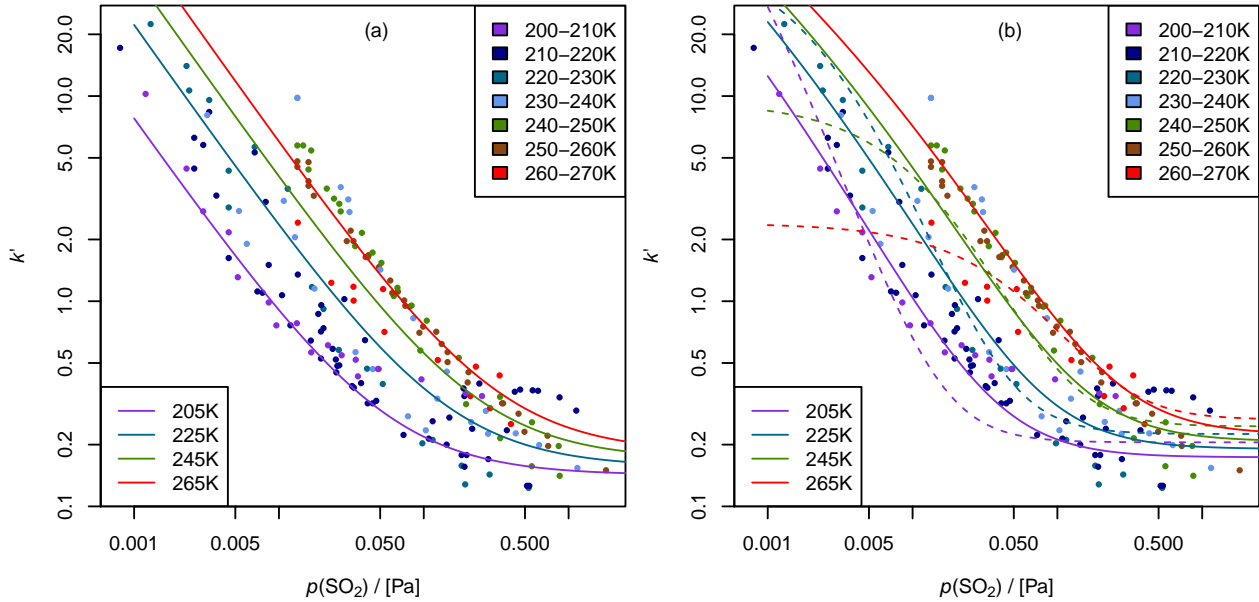


Figure 3. Double logarithmic plot of k' vs. $p(\text{SO}_2)$ at peak maximum for experiments with ice film thickness $h > 4 \mu\text{m}$ and without ice aging. (a) Fit with Temkin adsorption isotherm according to Eq. (7). (b) Fit with simple Langmuir model (dashed lines) according to Eq. (10) and with the dissociative Langmuir model (solid curves) according to Eq. (16).

~~For the transition between the high and low concentration limits we assume~~ Together with the weaker physisorption described by Henry's adsorption isotherm of Eq. (4), it follows that

$$k' = \frac{2RT}{r} \left(\frac{\zeta}{p} + K_H \right). \quad (7)$$

~~to be valid.~~ Note that only the model parameter ζ of the Temkin isotherm can be determined from concentration dependent k' -measurements. This is because the second model parameter K_T is arbitrarily removed by differentiation of Eq. (5). The linear relationship of k' vs. $1/p$ is used to study the relationship between film thickness, temperature, pre-humidification and column aging which are treated as independent variables by multiple linear regression using data from 336 chromatograms. Since the retention times at lower concentrations are difficult to obtain due to considerable peak broadening, the obtained k' are weighted with $1/k'$ in the linear regression. The results indicate that k' significantly increases with increasing temperature ($P < 0.01$), column aging ($P < 0.01$) and ice film thickness ($P = 0.03$). Therefore, further analysis is confined to a subset of 249 experiments with ice film thickness $h > 4 \mu\text{m}$. All these experiments were performed using pre-humidified carrier gas. In this subset, k' significantly increases with temperature ($P < 0.01$) and column aging ($P < 0.01$) but not with ice film thickness ($P = 0.81$). A linear dependency ~~of~~ on ζ from T and column aging is formulated, see Table 1. Next, the fit parameters are determined by nonlinear regression of the log-scaled data, see Fig. 3a. The residuals of the fit are normal distributed (Shapiro-
15 Wilk normality test, $P = 0.19$).

Langenberg (1997) applied a Langmuir adsorption model for the chemisorption in addition to a Henry's adsorption isotherm for weak physisorption. The Langmuir-isotherm is defined by the expression

$$\theta = \frac{q}{q_S} = \frac{(K_L/q_S)p}{1 + (K_L/q_S)p}, \quad (8)$$

5 $(K_L) \equiv \text{mol m}^{-2} \text{Pa}^{-1}$ where q_S is the monolayer saturation capacity. For K_L , a van't Hoff like temperature dependency was assumed. For low p where $(K_L/q_S)p \ll 1$ the Langmuir-model simplifies to the Henry's adsorption isotherm $q \approx K_L p$. By applying Eq. (1) to the Langmuir-model of Eq. (8), we form

$$k' = \frac{2RT}{r} \frac{K_L q_S^2}{(K_L p + q_S)^2} \quad (9)$$

and by adding Henry's law adsorption isotherm arithmetic expression for independent weak physisorption one obtains

$$k' = \frac{2RT}{r} \left(\frac{K_L q_S^2}{(K_L p + q_S)^2} + K_H \right). \quad (10)$$

10 When fitting this model to the log-scaled data, the dashed lines in Fig. 3b are obtained with the model parameters listed in Table 1. From these model parameters, an apparent adsorption enthalpy of $\Delta H_a = -(41 \pm 3) \text{ kJ mol}^{-1}$ is estimated. As can be seen in Fig. 23b, the fit is quite good at lower temperatures but fails at higher temperatures. When comparing the fit to those of the Temkin model, it is obvious that the Langmuir-model is not appropriate.

15 Clegg and Abbatt (2001) proposed a model for the adsorption of SO_2 where SO_2 interacts with the ice surface by hydrolyzing, as it does when being dissolved in liquid water. The equilibrium of the first dissociation step of SO_2 in water (see R1) is described by

$$K_{I1} = \frac{q(\text{H}_3\text{O}^+)q(\text{HSO}_3^-)}{q(\text{SO}_2)} \quad (11)$$

On neutral ice, where $q(\text{HSO}_3^-) = q(\text{H}_3\text{O}^+)$, the surface concentration of S_{IV} is given by

$$q(\text{S}_{\text{IV}}) = q(\text{HSO}_3^-) + q(\text{SO}_2) \quad (12)$$

$$20 \quad = \sqrt{K_{I1} K_H p} + K_H p. \quad (13)$$

Together with Eq. (1), we arrive at

$$k' = \frac{2RT}{r} \left(\frac{1}{2} \sqrt{\frac{K_H K_{I1}}{p}} + K_H \right). \quad (14)$$

This model yields a dependence of $k' \propto p^{-1/2}$ in the low concentration regime, but not for our data which were obtained at much higher concentrations than those used by Clegg and Abbatt (2001).

25 In cases where an adsorbing molecule dissociates upon adsorption the Langmuir isotherm takes a modified form (Crowley et al., 2010; Huthwelker et al., 2006):

$$\theta = \frac{q}{q_S} = \frac{\sqrt{\frac{K_H K_{I1} p}{q_S^2}}}{1 + \sqrt{\frac{K_H K_{I1} p}{q_S^2}}}. \quad (15)$$

With Eq. (1) and adding the Henry-adsorption term, it follows that

$$k' = \frac{2RT}{r} \left(\frac{\frac{K_H K_{I1}}{q_S}}{2\sqrt{\frac{K_H K_{I1} p}{q_S^2}} \left(\sqrt{\frac{K_H K_{I1} p}{q_S^2}} + 1 \right)} + K_H \right). \quad (16)$$

Model parameters $K_H K_{I1}$ and q_S are determined by nonlinear regression. No temperature dependency of $K_H K_{I1}$ is found. The dependency q_S from temperature is formulated by a van't Hoff like expression, see Table 1. In addition, q_S is about 60% larger for aged ice. However, the residuals of the fit are not normal distributed (Shapiro-Wilk normality test, $P = 0.04$).

Due to strong scatter, we are not able to find a significant temperature trend for K_H describing the physisorption of SO_2 . To explore the temperature dependency of K_H , temperature dependent measurements of k' were performed using higher concentrations with a partial pressure of around $p(\text{SO}_2) = 1$ Pa at the recorded peak maximum. In addition, the experimental setup was changed: instead of using the methylsilyl-deactivated column, an untreated fused silica column was used. We assumed that due to better wettability, ice deposition on the untreated silica surface results in a better surface coverage than in methylsilyl-deactivated columns. Furthermore, the coating procedure in these subsets of experiments was modified to minimize the length of the uncoated part of the column inside the cold box: after preparing the coating as described above, the cold box was opened and the uncoated tail of the column was manually drawn out of the box through a pinhole. This reduced the length of the uncoated tail in the cold box to about 30 cm. For further stabilization of the ice surface, the column was maintained for 3 h at 256 K after the coating procedure. After keeping the column at 207 K overnight, the chromatographic experiments were performed the next day. The ice film thickness was $6.5 \mu\text{m}$. To find evidence for anomalous adsorption behavior of SO_2 caused by the formation of a quasi-liquid layer when approaching the melting point of water ice, the SF_6/SO_2 chromatograms were measured up to 267 K. If a surface premelt layer acted like a supercooled liquid water film, SO_2 might dissolve in the layer therefore enhancing the capacity ratio k' and therefore K_H when approaching the melting point. However, with one exception where the column erroneously had not been rinsed before with Milli-Q water and dried with synthetic air to remove soluble impurities, mainly NO_3^- -ions, SF_6 and SO_2 peaks could not be separated at temperatures > 232 K. This implies that our results obtained with the untreated column are unaffected by a quasi-liquid layer at higher $p(\text{SO}_2)$ where k' is nearly independent of $p(\text{SO}_2)$. The results indicate that the dominant adsorption at higher $p(\text{SO}_2)$ which was probed in our experiments is physisorption on the dry surface. In those cases where the measured peaks of SF_6 and SO_2 overlap the true peak maxima were determined by fitting two exponential modified Gauss functions to the overlapping peaks (Felsing, 1994). Afterwards the peak maximum time of each peak was determined by a linear search algorithm. K_H at $p \rightarrow \infty$ is determined as intercept by linear regression of k' vs. p^{-1} using Eq. (7). In Fig. 4 the Henry's law adsorption constant $\ln K_H$ obtained for ice coated methylsilyl-deactivated columns and an ice coated untreated column are plotted against $1/T$. With van't Hoff equation

$$\ln K_H = \ln K_H^\infty - \frac{\Delta H_a}{RT} \quad (17)$$

no reasonable fit is possible for the experiments performed with methylsilyl-deactivated columns. Even in the case of the untreated column, the values of K_H systematically deviate from the van't Hoff plot regression line. Whereas K_H is weakly dependent of temperature using the methylsilyl-deactivated fused silica column, K_H decreases more strongly with tempe-

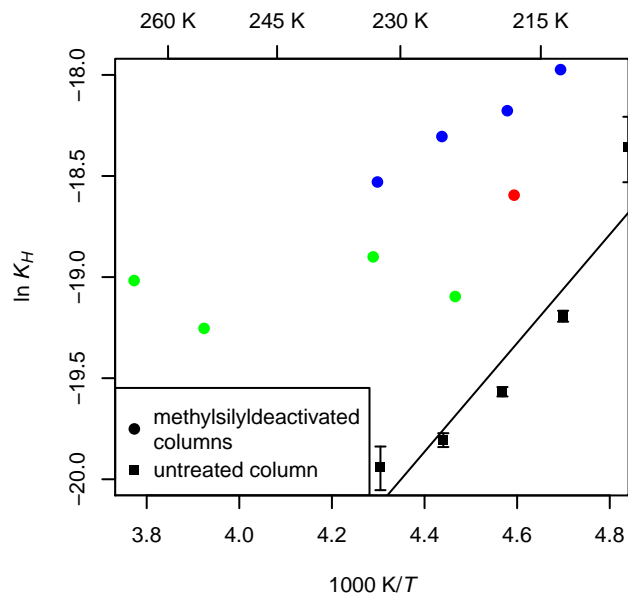


Figure 4. K_H as function of T for experiments using an untreated column and methylsilyl-deactivated columns coated with aged ice. Experiments conducted with the same prepared column are marked by the same color.

perature than when using an untreated fused silica column. A possible explanation for this might be that at higher temperatures formation of a quasi-liquid layer occurs at the interface of ice with the methylsilyl-deactivated fused silica surface.

3.2 Adsorption of acetone and n -hexane

To explore the possible impact of a quasi-liquid layer, the adsorption of acetone and n -hexane on an ice coated methylsilyl-deactivated column was probed in the temperature range 211 - 265 K. These compounds were selected because they are comparable in vapor pressure over a wide temperature range but differ in water solubility: n -hexane is insoluble in water, whereas acetone is ~~mixable~~ miscible with water. Methane was used as inert tracer. Fig. 5 shows the chromatograms obtained using a methylsilyl-deactivated column coated with an ice film of $7.1 \mu\text{m}$ thickness. From left to right, the recorded peaks are from methane, n -hexane, and acetone. The n -hexane peaks are nearly symmetrical and the retention times are independent ~~of~~ on the amounts injected, whereas the acetone peaks show some tailing with slightly increasing retention times with decreasing injection amounts, indicating that the slope of the isotherm is nonlinear. The adsorption of acetone on ice is described by a Langmuir adsorption isotherm according to Eq. (8), see review of Crowley et al. (2010). Eq. (9) is reorganized into a linear relation of $1/\sqrt{k'}$ vs. p :

$$\sqrt{\frac{2RT}{rk'}} = \frac{\sqrt{K_L}}{q_S} p + \frac{1}{\sqrt{K_L}}. \quad (18)$$

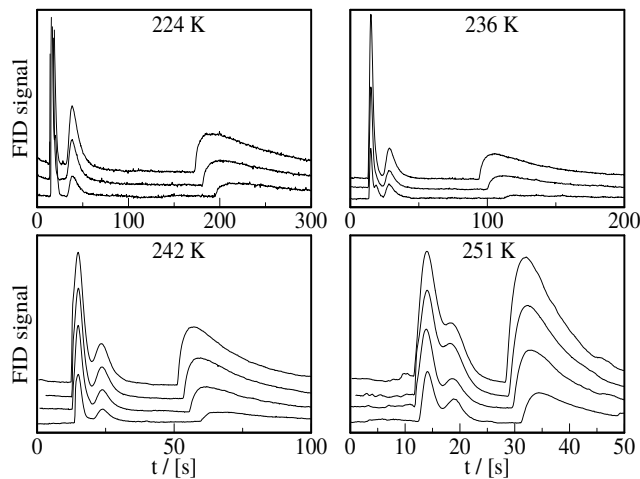


Figure 5. Chromatograms of a mixture of methane, *n*-hexane and acetone at different temperatures. Flow rate 10 sccm. Methane is used as non adsorbable tracer.

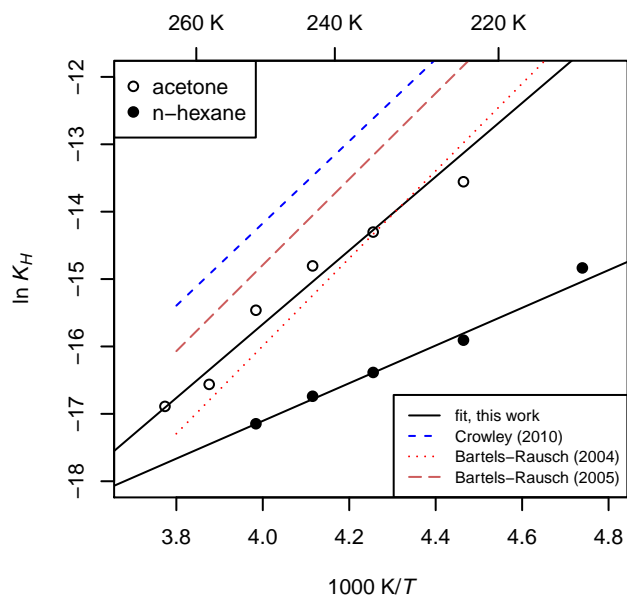


Figure 6. Van't Hoff plot of $\ln K_H$ vs. inverse temperature for adsorption of acetone and *n*-hexane on ice using a methylsilyl-deactivated fused silica column. The solid lines are fits of the data to Eq. (17), used to derive adsorption enthalpies. Van't Hoff plots of acetone from Bartels-Rausch et al. (2004a, b) and Bartels-Rausch et al. (2005) and recommended values from Crowley et al. (2010) extrapolated from lower temperatures to the temperature range investigated are shown for comparison.

Table 2. Adsorption isotherm of *n*-hexane and acetone on ice

	$\ln(K_H^\infty/1) - \ln(K_H^\infty/1) \text{ mol m}^{-2} \text{ Pa}^{-1}$	ΔH_a [kJ mol ⁻¹]
<i>n</i> -hexane	-28.3 ± 0.9	-23 ± 2
acetone	-37.6 ± 2.5	-45 ± 5

K_L of acetone is determined after linear regression from the intercept. For *n*-hexane, mean values of the retention times are determined for different injection amounts at one temperature. K_H of *n*-hexane is calculated using Eq. (4). The enthalpies of adsorption are determined using Eq. (17) by linear regression, see Fig. 6 and Table 2.

4 Discussion

5 4.1 Consistency of the peak maxima method

The consistency of the peak maxima method is checked by theoretical peak shape calculations, see supplement S2 and Fig. 2b. When comparing locations of experimental peak maxima with peak maxima predicted by Eq. (1), it can be seen that at higher concentrations, the peak maxima are shifted towards longer retention times. As stated by Jönsson and Lökvist (1987), for Langmuir-like adsorption isotherms the accuracy of the peak maxima method is best for low to moderate concentrations.

10 Hence, in case of nonlinear adsorption, the isotherm determined by the peak maxima method at higher concentration has to be regarded as upper limit.

Slow uptake of SO₂ by diffusion into the ice surface is included into the 2D model, see Fig. 2b. When taking diffusion into the ice surface into account, the peak maxima are shifted on the curve of Eq. (1) to higher retention times. In addition, the peak maxima are smaller and tailing is enhanced. As can be seen from the simulation without including slow uptake (1D model),
 15 Eq. (1) is nearly the envelope of the tails of the simulated peaks. This is used by the *peak profile method* (Huber and Gerritse, 1971) to determine the slope of the isotherm from a single peak tail. But, due to slow uptake into the surface, this method is not applicable for SO₂ on ice.

4.2 Comparison with literature

4.2.1 Adsorption of SO₂

20 The reanalysis of our experimental data reveals that the simple Langmuir adsorption isotherm is not suitable for the description of adsorption of SO₂ on ice. Only considering our data, either the Temkin model or the dissociative Langmuir model are more appropriate. When taking the results of Clegg and Abbatt (2001) and the chemical nature of SO₂ into account, we conclude that the adsorption is best described by the dissociative Langmuir model of Eq. (15) combined with simple physisorption described by Henry's adsorption isotherm. The experiments of Clegg and Abbatt (2001) were performed at lower SO₂ concentrations,

thus saturation effects were not observed. SO₂ reaction with ice and dissociation is also supported by the study of Jagoda-Cwiklik et al. (2008) who investigated SO₂ adsorbates on the surface of ice nanoparticles at 128 K by FTIR spectroscopy: like in aqueous solutions, an HSO₃⁻ ion was found.

5 Crowley et al. (2010) reported a value of $K_{I1}K_H = 1.3 \times 10^{-13} \text{ mol}^2 \text{ m}^{-4} \text{ Pa}^{-1}$ based on the data of Clegg and Abbatt (2001) for the model of Eq. (13) at 228 K. This value lies within the error limit of our value of $K_{I1}K_H = (7 \pm 5) \times 10^{-14} \text{ mol}^2 \text{ m}^{-4} \text{ Pa}^{-1}$. A limitation of our study is that the experiments were performed at rather high SO₂ concentrations. This makes the determination of $K_{I1}K_H$ rather difficult, as can be seen by a value of $P = 0.1$ for this fit parameter, see Table 1. Therefore, we are not able to find a temperature trend for $K_{I1}K_H$. This is in contrast to the observation of Clegg and Abbatt (2001) who found less uptake at lower temperatures.

10 The monolayer saturation capacity q_S of the dissociative Langmuir model describes the maximal adsorbed amount of SO₂ in one monolayer. Our values range from $9 \times 10^{-9} \text{ mol m}^{-2} \triangleq 5 \times 10^{11} \text{ cm}^{-2}$ at 205 K to $4 \times 10^{-8} \text{ mol m}^{-2} \triangleq 2 \times 10^{12} \text{ cm}^{-2}$ at 265 K, see Table 1. Clegg and Abbatt (2001) estimated that about $5 \times 10^{14} \text{ cm}^{-2}$ molecules of the size of SO₂ can be packed on the surface next to each other. For small molecules a saturation capacity of $2.2 \times 10^{14} - 4.5 \times 10^{14} \text{ cm}^{-2}$ was found experimentally (Crowley et al., 2010). Taking $5 \times 10^{14} \text{ cm}^{-2}$ as reference, dissociative adsorption of SO₂ must occur on active
15 sites representing 0.1% - 0.5% of the total surface. This result may be explained by surface premelting. At temperatures close to the melting point the ice surface may be regarded as a quasi liquid layer where the hexagonal oxygen lattice is completely distorted. At temperatures below ≈ 260 K the oxygen lattice is distorted by point defects and the hydrogen-bond network is distorted. Either vacancies in the outer bilayer predicted by molecular dynamics simulations (Bishop et al., 2009; Riikonen et al., 2014) or Hydronium, hydroxide, and the Bjerrum L- and D-defects predicted by density functional theory calculations
20 (Watkins et al., 2010) prevailing at the surface come into question as active sites for dissociative adsorption. D-defects at the surface, bearing a positive charge, possibly could attract HSO₃⁻-ions at the surface. Watkins et al. (2010) found by density functional calculation that surface D-defects form with a very small energy penalty of 0.06 eV. From model parameter a_2 describing the temperature dependency ~~of~~ on q_S , an activation energy of $11 \text{ kJ mol}^{-1} \triangleq 0.11 \text{ eV}$ for the formation of an active site can be derived. Surprisingly for the hypothetical case of $T \rightarrow \infty$ K the saturation capacity approaches a limit of
25 $q_s = 3 \times 10^{14} \text{ cm}^{-2}$.

One unanticipated finding is that q_S is larger for aged ice. A possible explanation for this might be that surface defects are more prevalent on the surface of aged ice. Another possible explanation for this is that the ice surface in our capillary columns increases during aging: shortly after preparation of the column, the inner wall is covered with individually frozen drops of water. During aging, the interstitial ice-free surface of the column is eventually covered with ice by desublimation from the
30 frozen drops.

Besides the aging effect, other reasons for poor reproducibility of the properties of ice surfaces must exist. Whereas the reproducibility of the chromatograms of one column at one temperature is good, the reproducibility of experiments of two prepared columns is rather bad. There are several possible explanations for this result: the properties of the ice surface is also affected by the underlying surface properties of the fused silica column, which may influence crystallinity and surface defects.

4.2.2 Adsorption of acetone and *n*-hexane

In recent years, several studies concerning the adsorption of acetone on ice have been published, see the review of Crowley et al. (2010) and references therein. However, all these studies only covered the temperature range of 140–228 K. In this review, the results are summarized as an expression for the van't Hoff equation for Henry's law adsorption isotherm using Eq. (17). When
5 extrapolating these expressions to the higher temperature range of our experiment, it is found that the isotherms of Bartels-Rausch et al. (2004a, b) and Bartels-Rausch et al. (2005) are closest to our measured values of Henry's adsorption isotherm constant, see Fig. 6. In the first study, breakthrough curves were measured using a column packed with ice beads and in the second study an ice coated-wall flow-tube was used. Bartels-Rausch et al. (2004a) and Bartels-Rausch et al. (2005) obtained an adsorption enthalpy of $-52 \pm 2 \text{ kJ mol}^{-1}$ and $-46 \pm 3 \text{ kJ mol}^{-1}$, respectively. Our value of $-45 \pm 5 \text{ kJ mol}^{-1}$ is slightly
10 lower but complies within the error limits.

Bartels-Rausch et al. (2004a) determined the surface area available for adsorption by a BET analysis of methane adsorption isotherms. Bartels-Rausch et al. (2005) prepared the ice surface by slowly freezing water at the inner surface of a Pyrex flow-tube. They assume that the ice surface corresponds to the geometric inner surface of the tube. Thus, in both experiments the surface of ice adsorbents is regarded to be known. These results suggest that within experimental uncertainty, the real ice
15 surface in our column corresponds approximately to the geometric inner surface of the ice coated part of the column, due to the consistency of our data concerning the adsorption of acetone with these studies. The temperature trend of the isotherms of Bartels-Rausch et al. (2004a) and Bartels-Rausch et al. (2005) extrapolates to higher temperatures up to 265 K. No visible change caused by a quasi-liquid layer is found in the temperature trend.

For *n*-hexane on pure ice, the enthalpy of adsorption has not been measured yet. Hoff et al. (1995) reported $\Delta H_a = -37.3 \pm$
20 1.3 kJ mol^{-1} for the adsorption on ice-coated Chromosorb P in the temperature range 263–273 K, which is much higher than our value of $-23 \pm 2 \text{ kJ mol}^{-1}$. For adsorption of *n*-hexane on liquid water -28 kJ mol^{-1} were determined by Hartkopf and Karger (1973) at 286 K.

4.3 Atmospheric implications

The adsorbed fraction of a trace gas in a contrail or cirrus cloud with ice surface area density σ is given by

$$25 \quad \frac{N_s}{N_g} = \frac{\sigma RT q}{p}. \quad (19)$$

In case of Henry's adsorption isotherm of Eq. (3), we can write

$$\frac{N_s}{N_g} = \sigma RT K_H. \quad (20)$$

In case of the model Eq. (13) and of the dissociative Langmuir model of Eq. (15), we arrive at

$$\frac{N_s}{N_g} \approx \sigma RT \sqrt{\frac{K_{I1} K_H}{p}} \quad (21)$$

30 at low concentrations. For cirrus clouds $\sigma = 0.003 \text{ m}^{-1}$ and for contrails $\sigma = 0.003 - 0.012 \text{ m}^{-1}$ were reported by Schröder et al. (2000). In an aircraft plume SO_2 -concentrations of $> 5 \times 10^8 \text{ cm}^{-3}$ were observed by Schumann et al. (1998). At 205 K

the adsorbed fraction calculated with Eq. (21) is about 10^{-3} for $\sigma = 0.003 \text{ m}^{-1}$. For acetone the adsorbed fraction according to Eq. (20) is about 10^{-4} at 205 K. These findings suggest that adsorption of SO_2 and acetone on ice particles in the plume of an aircraft and subsequent vertical transport by particle sedimentation is negligible.

Sokolov and Abbatt (2002) estimated an upper limit for the surface density of $\sigma = 0.1 \text{ m}^{-1}$ for tropospheric ice clouds. Here, the adsorbed fraction of SO_2 is about 0.3 at the same SO_2 concentration as above. Therefore, we conclude that interaction of SO_2 with ice is only important in very dense ice clouds.

5 Conclusions

Gas-chromatography with water-ice coated fused silica ~~column~~ columns is a well suited screening tool to study adsorption of trace gases with weak or medium adsorption in the range $k' = 0.1 - 100 \triangleq K_H = 8 \times 10^{-9} - 8 \times 10^{-6} \text{ mol m}^{-2} \text{ Pa}^{-1}$. By using humidified carrier gas, the experiments can be performed at temperatures close below the melting point. Excepting the special low temperature coating box, only standard equipment for gas chromatography is required.

The interaction of SO_2 with ice surfaces in the temperature range 205 – 265 K is described by a dissociative Langmuir-model in conjunction with weaker physisorption described by Henry's adsorption isotherm. No temperature trend for the adsorption equilibrium constant is found for the dissociative adsorption process. The monolayer saturation capacity for dissociative adsorption increases with increasing temperature and ice aging. Adsorption occurs on active sites representing 0.1% - 0.5% of the total surface. These findings support the existence of surface premelting.

Slow uptake into the ice surface is evidenced by peak tailing in addition to tailing arising from the nonlinear isotherm.

The possible interference of the underlying bare or methylsilyl-deactivated column surface with the ice surface cannot be ruled out. Further work is required to find evidence if ice films on untreated fused silica surfaces or on methylsilyl-deactivated fused silica surfaces are more likely resembling the surface of atmospheric ice particles.

Code availability. The R-code for simulation of chromatograms is provided as supplement.

Author contributions. U.S. suggested the experimental setup. S.L. performed the experiments, analyzed the data, and drafted the manuscript.

Competing interests. The authors declare that they have no conflict of interest.

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