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The Uptake of SO_2 on Synthetic Sea Salt and Some of Its Components

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Abstract. The uptake of sulfur dioxide (SO_2) on synthetic sea salt (SSS) and its components, NaCl and $MgCl_2 \cdot 6H_2O$, was studied at 298 K using a Knudsen cell interfaced to a quadrupole mass spectrometer. Significant uptake on dried salts was not observed, placing upper limits on the uptake coefficients, γ, of < 1×10^{-4} for NaCl, < 5×10^{-4} for $MgCl_2 \cdot 6H_2O$, and < 8×10^{-5} for SSS. However, SSS and $MgCl_2 \cdot 6H_2O$ that had not been dried before use showed significant uptake of SO_2. The magnitude of the uptake depended strongly on the exposure time and the amount of water desorbing. Initially, the measured uptake coefficients for SO_2 on SSS were as high as 0.09, but they rapidly decreased below 10^{-2} with a $t^{-1/2}$ dependence as expected for approach to the equilibrium saturation concentration in an aqueous solution. The decreasing uptake coefficient slowly approaches zero over hours, consistent with reactions in a water layer with species such as $CaCO_3$. The products of the reaction were shown by diffuse reflectance IR Fourier transform spectroscopy (DRIFTS) to include low solubility metal sulfites. These studies show that uptake of SO_2 on sea salt particles, even below their deliquescence/effluorescence points, can be treated as if it is into an aqueous salt solution.

1. Introduction

Sulfur dioxide (SO_2) in the marine boundary layer is oxidized in deliquesced sea salt aerosol with dissolved oxidants such as ozone and H_2O_2 to form S(VI) species [*Luria and Sievering*, 1991; *Sievering et al.*, 1991, 1992, 1995; *Chameides and Stelson*, 1992; *Suhre et al.*, 1995; *Keene et al.*, 1998; *Capaldo et al.*, 1999]. In addition, HOCl and HOBr have been proposed as potential oxidants for dissolved SO_2 in sea salt particles [*Vogt et. al.*, 1996]. Field studies show that aged sea salt aerosol routinely has amounts of sulfate in excess of what would be expected for aerosol freshly generated from the ocean [e.g. *Pszenny et al.*, 1990]. This is consistent with oxidation of S(IV) from the gas phase to S(VI) in the particles [*Sievering et al.*, 1990, 1991, 1995]. Atmospheric sulfate particles can affect climate globally [*Lin et al.*, 1992; *Raes and Van Dingenin*, 1992, *Finlayson-Pitts and Pitts*, 2000], and are removed by wet and dry deposition, causing negative impacts on plant and animal life.

After gas phase transport to the surface, SO_2 is taken up into the particle, which is initially described by mass accommodation. Continuous uptake is then controlled by its solubility and reactions of S(IV) species in the aqueous phase. Mass accommodation coefficients have been measured for SO_2 on

water, but to our knowledge, not on sea salt either below or above its deliquescence/effluorescence points. We report here experimental studies of the uptake of SO_2 on powders of synthetic sea salt (SSS) and two of its major components, NaCl and $MgCl_2 \cdot 6H_2O$, below their deliquescence points. We show that if these salt surfaces are free of large amounts of water, then no measurable uptake is observed. However, when SSS and $MgCl_2 \cdot 6H_2O$ have not been dried, significant uptake of SO_2 is observed. Furthermore, a large initial uptake is followed by smaller, long-term uptake consistent with reaction in water associated with the salts to form relatively insoluble sulfites.

2. Experimental

Experiments were performed in a glass Knudsen cell with a movable lid for covering the sample and is described in detail elsewhere [*Beichert and Finlayson-Pitts*, 1996]. Reactant gases were introduced into the cell from a glass gas-handling manifold through a stainless steel needle valve coated with halocarbon wax (Halocarbon Products, Series 1500). The Knudsen cell was interfaced to a quadrupole mass spectrometer (ABB Extrel, 150-QC) through a removable glass aperture (diameters 3.9 or 5.8 mm). Ion current signals from the SO_2^+ and H_2O^+ parent ions were obtained by phase sensitive detection and processed with a lock-in amplifier (EG&G, Model 5209) interfaced to a PC running data acquisition software (ABB Extrel, Merlin, rev. B).

In the Knudsen cell, reactant gas molecules can be lost through the small exit aperture or by uptake by the sample. A net uptake coefficient, γ_{net}, can be determined from the ratio of the effusive loss through the exit aperture to the loss on the surface. The measured uptake coefficient was derived from the relation:

$$\gamma_{net} = \frac{(I_o - I_r)}{I_r}\left(\frac{A_{hole}}{A_{surf}}\right)$$

I_0 is the steady-state reactant signal at the mass spectrometer with the surface covered, and I_r is the reactant signal when the reactive surface is exposed to the gas. A_{surf} is the reactive surface area taken to be the geometric surface area of the sample holder, 7.5 cm^2, and A_{hole} is the area of the exit aperture.

The salts in these studies were obtained commercially: NaCl (Bicron, single crystals), synthetic sea salt (Instant Ocean), and $MgCl_2 \cdot 6H_2O$ (Sigma, ACS Reagent). Grinding and sieving yielded coarse particles with diameters between 425 and 850 microns. Mechanical grinding in a Wig-L-Bug amalgamator (Crescent Dental) yielded fine particles between 0.1-10 microns in diameter [*Vogt and Finlayson-Pitts*, 1994; *Langer et al.*, 1997]. Dried salts are those that have been placed in an oven (100° C) overnight. Salts were baked and pumped under vacuum to control the amount of water associated with the salt prior to exposure to SO_2. At the beginning of each experiment, the

Knudsen cell was pumped to a base pressure on the order of mTorr with the salt sample uncovered. The salt was then covered and the cell was pumped further. When synthetic sea salt or $MgCl_2 \cdot 6H_2O$ that was not dried was subsequently uncovered, considerable amounts of water were released before exposure to SO_2. After heating at 80° C under vacuum for 1-5 hours, the water signal reached a constant value. Sodium chloride holds much less water, so it could be rapidly pumped down to a constant (background) water signal with or without prior drying. Anhydrous SO_2 (Matheson, 99.98%) was used as received.

Diffuse Reflectance IR Fourier Transform Spectroscopy (DRIFTS) was used to probe for possible surface bound products of reaction on the salts [Griffiths and Fuller, 1982]. Fine SSS was prepared for DRIFTS studies by grinding in the Wig-L-Bug amalgamator for 3 minutes. Immediately after grinding, the salt was packed into a stainless steel cup (13 mm diameter, 2 mm height) using a device like that described by TeVrucht and Griffiths [1989]. Samples were exposed to SO_2 gas in a small chamber equipped with ZnSe windows and placed within a SpectraTech "Collector" diffuse reflectance accessory. Mid-IR spectra were obtained at 4 cm^{-1} resolution on a Nicolet 740 FTIR spectrometer using a wide-band MCT detector.

3. Results

Initial experiments performed using dried salts showed no release of gas phase water from the surface and no net uptake of SO_2. Upper limits on the uptake coefficients for SO_2 on the dry salt powders were estimated by setting the change in intensity upon exposure equal to 3σ from a linear least squares fit to the unchanging reactant signal, I_o, of an experiment for each salt. These upper limits are 1×10^{-4} for NaCl, 5×10^{-4} for $MgCl_2 \cdot 6H_2O$, and 8×10^{-5} for SSS. In experiments using SSS or $MgCl_2 \cdot 6H_2O$ that was not dried prior to being put in the Knudsen cell, significant uptake of SO_2 was seen for long times, in contrast to NaCl where there was no such uptake. A typical intensity-time profile for SO_2 on SSS is shown in Figure 1. When the lid is opened there is a sharp drop in the SO_2 signal and an increase in the H_2O signal. An estimate of the amount of water available during the first 300 s was derived by integrating the water signal. As seen in Table 1, there is a large amount of water available for aqueous reaction on these salt powders. While some of it is likely strongly adsorbed water observed in previous studies [De Haan and Finlayson-Pitts, 1997], some may also be due to water trapped in cavities of the salt particles [Langer et al., 1997; Weis and Ewing, 1999a, 1999b]. Although NaCl contains some adsorbed water, the amount was not enough for measurable uptake under our experimental conditions.
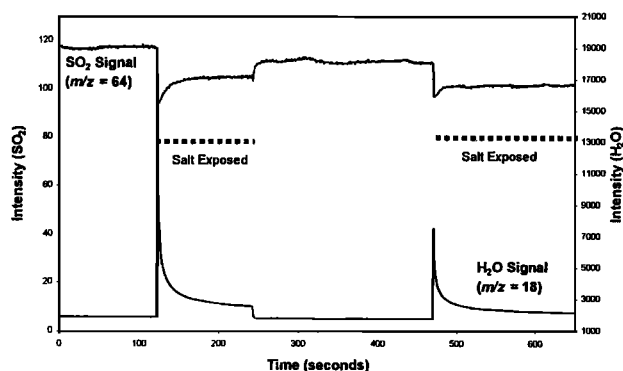

Figure 1. Uptake of SO_2 (left axis) and release of H_2O (right axis). Time at which lid remained open denoted by dashed line.

The magnitude of the SO_2 uptake has a strong time dependence during the first ~25 seconds, but smaller uptake continues for hours. This time dependence (Fig. 1) is qualitatively consistent with the uptake of SO_2 into an aqueous solution due to its solubility and reaction with components of sea salt such as $CaCO_3$; such behavior is consistent with earlier studies in which the salt surface was shown to behave much like a saturated salt solution with respect to the uptake and reaction of HNO_3 [De Haan and Finlayson-Pitts, 1997]. This suggests the application of a resistance model to the data often applied to the uptake of gases into aqueous solutions [e.g., Hanson et al., 1994; Kolb et al., 1995, 1997]. However, under our experimental conditions, there are varying amounts of water initially that change with time when the lid is opened, cooling as evaporation occurs. Thus, such an approach is semi-quantitative at best. However, it is useful for probing the liquid-like nature of the salt surface and how this controls the uptake and reaction of gases.

If diffusion of the gas to the surface is fast, the net uptake coefficient is approximated by eqn. (I):

$$\frac{1}{\gamma_{net}} = \frac{1}{\alpha} + \frac{1}{\Gamma_{sol} + \Gamma_{rxn}} \tag{I}$$

α is the mass accommodation coefficient; Γ_{sol} represents uptake due to solubility and is given by eqn. (II); Γ_{rxn} represents uptake due to reaction in the aqueous layer and is given by eqn. (III):

$$\Gamma_{sol} = [4H^*RT/c]\sqrt{D_l/\pi \cdot t} \quad (II) \qquad \Gamma_{rxn} = [4H^*RT/c]\sqrt{D_l \cdot k_{rxn}} \quad (III)$$

H^* is the effective Henry's Law coefficient; R is the gas constant; T is the temperature; c is the mean speed of the gas (for SO_2 at 298 K, $c = 3.1 \times 10^4$ cm s^{-1}); D_l is the liquid phase diffusion coefficient (for SO_2 in water at 298 K, $D_l = 1.8 \times 10^{-5}$ cm^2 s^{-1}) [Leaist, 1984]; and k_{rxn} (s^{-1}) is a pseudo-first order rate constant. An effective Henry's Law coefficient must be used for SO_2 because it reacts with water [Finlayson-Pitts and Pitts, 2000]:

$$
\begin{array}{lll}
SO_2 + H_2O \Leftrightarrow SO_2 \cdot H_2O & H = 1.24 \text{ M atm}^{-1} & (1) \\
SO_2 \cdot H_2O \Leftrightarrow HSO_3^- + H^+ & K_1 = 1.32 \times 10^{-2} \text{ M} & (2) \\
HSO_3^- \Leftrightarrow SO_3^{2-} + H^+ & K_2 = 6.42 \times 10^{-8} \text{ M} & (3)
\end{array}
$$

H^* for SO_2 is given by equation (IV):

$$H^* = H\left(1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}\right) \tag{IV}$$

Values for H^* range from 1.2×10^7 M atm^{-1} at pH = 8.0, characteristic of sea water, to that for physical solubility in strongly acidic solutions, $H^* \rightarrow 1.24$ M atm^{-1}.

The behavior of the SO_2 upon first exposing the salt (t → 0) is controlled by physical transport across the gas-liquid interface, i.e., $\gamma_{net}^{t \rightarrow 0} = \gamma_{init} \rightarrow \alpha$. The values of the uptake coefficient measured immediately after exposure, γ_{init}, for SSS and $MgCl_2 \cdot 6H_2O$ (not dried) are summarized in Table 1. These values range from 0.006 to as high as 0.09. The highest values of γ_{init} approach those reported for SO_2 on water at room temperature, which vary from 0.028 ± 0.010 to 0.13 ± 0.01 [Worsnop et al., 1989; Ponche et al., 1993; Shimono and Koda, 1996]. If the subsequent decrease in the initial uptake (Fig. 1) is due to the water becoming saturated with SO_2, $1/\gamma_{net}$ should show a $t^{1/2}$ dependence. As seen in Figure 2, this is indeed the case. Average values of H^* can be derived from the slopes of such plots, and hence from eq. (IV), the average pH. Values of pH between 5.4 and 6.6 are derived, consistent with acidification by reactions (1)-(3). It should be emphasized that the surface
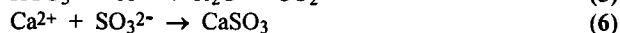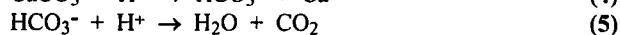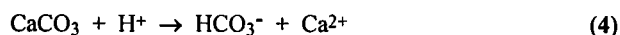
Table 1. Summary of Uptake of SO_2 on SSS and $MgCl_2 \cdot 6H_2O$ which has not been dried prior to experiment.

Exp.[a]	γ_{init}[b]	γ_{ss}[b]	salt type	$[SO_2]$ (molec. cm^{-3})	salt weight (g)	particle layers[c]	H_2O released in 300 s (μL) ($\pm 2\sigma$)[d]
1	0.090	0.0061	coarse	1.6×10^{13}	1.21	1.5	2.0 ± 0.3
2	0.059	0.0081	coarse	1.9×10^{13}	0.92	1.1	2.3 ± 0.2
3	0.057	0.0062	coarse	1.9×10^{13}	0.89	1.1	2.0 ± 0.2
4	0.064	0.017	coarse	2.6×10^{13}	0.88	1.1	8.1 ± 0.5
5	0.023	0.0077	coarse	5.5×10^{13}	0.96	1.2	2.0 ± 0.11
6	0.013	0.0035	coarse	5.5×10^{13}	0.75	0.9	0.5 ± 0.1
7	0.017	0.0046	coarse	1.6×10^{13}	0.88	1.1	0.8 ± 2.0
8	0.0069	0.0018	coarse	1.9×10^{13}	3.45	1.7	n/a[e]
9	0.010	0.005	fine	0.3×10^{13}	2.06	253	2.5 ± 0.4
10	0.0060	0.0032	fine	2.1×10^{13}	1.72	210	1.1 ± 0.2
11	0.012	0.0040	fine	1.0×10^{13}	1.18	144	1.7 ± 0.2
12[g]	0.0077	0.0006	coarse	4.2×10^{13}	3.01	199	n/a[e]
13[g]	n/a[f]	0.0016	coarse	1.6×10^{13}	1.15	195	n/a[e]

[a] Aperture diameter for experiments 1-4 and 9-11 was 5.8 mm; for all others, 3.9 mm. [b] Determined assuming A_{surf} = geometric surface area, supported by the fact that increasing the number of salt layers does not significantly increase the measured uptake. However, actual surface area of the water available for uptake is likely less, making measured values less than true values. [c] Number of particle layers estimated using density of NaCl for SSS. [d] Error derived from linear least squares fit of signal calibration. [e] Water was not monitored. [f] This salt was pumped on, in the cell, overnight before expt., so no fast initial uptake observed. [g] $MgCl_2 \cdot 6H_2O$ was used in expts. 12-13.

water is a dynamic system and hence such an approach is at best a semi-quantitative description of the average conditions during initial uptake of SO_2. However, it is consistent with expectations for uptake into a liquid, rather than reaction with a solid surface, confirming the important role of water even for sea salt below its deliquescence/effluorescence point.

Although the uptake levels off at low values after long exposure (Fig. 1), it does not become zero as long as surface water is present. This is consistent with a slow reaction of S(IV) in the water layer. Sea salt is known to contain buffering species such as carbonates which can react with dissolved S(IV) [Sievering et al., 1991, 1992, 1995; Chameides and Stelson, 1992]:

$$CaCO_3 + H^+ \rightarrow HCO_3^- + Ca^{2+} \qquad (4)$$
$$HCO_3^- + H^+ \rightarrow H_2O + CO_2 \qquad (5)$$
$$Ca^{2+} + SO_3^{2-} \rightarrow CaSO_3 \qquad (6)$$

No gas phase products were observed in the Knudsen cell experiments. The possibility of the generation of surface-bound reaction products was probed using DRIFTS. A typical DRIFT spectrum of SSS after exposure to SO_2 is shown in Figure 3a. The band near 1360 cm^{-1} (v_3) is due to unreacted SO_2, and CO_2 is observed by its asymmetric stretching band near 2350 cm^{-1}. The negative features near 1450 cm^{-1} indicate a loss of carbonate (v_3 mode split by crystal site interactions) and the broad negative
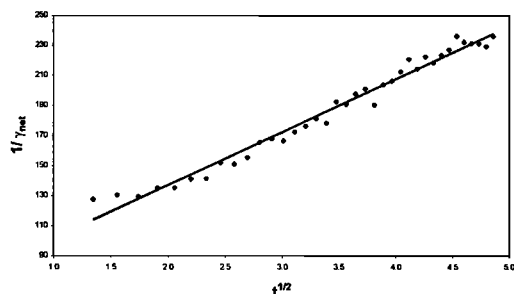
absorbance around 1650 cm^{-1} is due to a loss of water. DRIFTS was not used to quantify the amount of water due to the possible non-linear relationship between concentration and absorbance which arises from DRIFTS sensitivity to variations in particle size, packing density and pressure above the sample [Fuller and Griffiths, 1978]. A broader, featureless band near 960 cm^{-1} grows with time. This band is assigned as the v_1 vibration of sulfite, based on comparison to the DRIFT spectrum of anhydrous calcium sulfite (Figure 3b) which was synthesized in situ by passing SO_2 gas through neat calcium oxide [Martin et al., 1987]. In short, the net uptake of SO_2 at longer times (Fig. 1) is consistent with reactions such as (4)- (6) occurring in the water associated with the salt.

4. Conclusions

Uptake of sulfur dioxide on dry NaCl, synthetic sea salt, and $MgCl_2 \cdot 6H_2O$ is slow, with upper limits for the uptake coefficient of 1×10^{-4} for NaCl, 5×10^{-4} for $MgCl_2 \cdot 6H_2O$, and 8×10^{-5} for SSS. Significant uptake of SO_2 occurs into water associated with synthetic sea salt and $MgCl_2 \cdot 6H_2O$ which have not been dried.
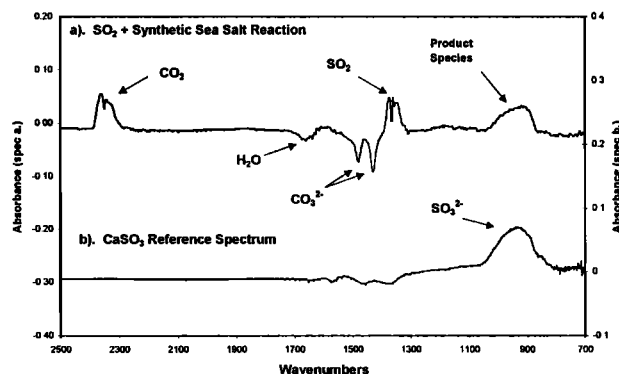
Figure 3. (a) DRIFTS spectrum of 15 Torr SO_2 over SSS for 2 hrs (right axis). Use of high concentration of SO_2 was necessary due to small fraction of carbonates in SSS and lower reflectivity of SSS, making detection of surface-bound products difficult. CO_2 peaks include reaction product plus CO_2 from incomplete sample compartment purge. (b) Reference spectrum for $CaSO_3$.

Figure 2. Variation of $1/\gamma_{net}$ with $t^{1/2}$ during the first 25 sec of exposure.

The uptake is due to the combination of dissolution and aqueous reaction. This behavior is similar to that which occurs in liquid atmospheric aerosols and is qualitatively consistent with a gas-liquid interaction resistance model. The aqueous reaction forms sulfites in the surface adsorbed water layer that may precipitate out as relatively insoluble salts such as $CaSO_3$. It is apparent that sea salt aerosol in the troposphere will contain enough water to behave like a liquid even at relative humidities below the deliquescence/effluorescence points and hence uptake of SO_2 may be treated in models as if particles have deliquesced, even under low relative humidity conditions.

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