LASER-SPECTROSCOPIC MEASUREMENT OF UPTAKE COEFFICIENTS OF TRACE GASEOUS SPECIES ON AQUEOUS SURFACES

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The transport of trace gaseous species from the bulk atmosphere across aqueous surfaces was studied in order to determine the relevant uptake coefficients. A direct observation of the distribution of the trace species in the gas phase above the surface between the gas and aqueous phase was conducted in an impinging flow field using a laser-spectroscopic detection technique. By analyzing the experimental results and comparing them to simulation results, the applicability of the present method to obtaining the uptake coefficients was demonstrated in the case of SO_2 .

Introduction

Heterogeneous reactions of trace species, particularly active species, on aerosol surfaces play very important roles in many aspects of atmospheric chemistry, particularly in the case of acid-rain formation in the troposphere, and in ozone depletion in the stratosphere. Gas absorption by liquids is also an essential step in the field of chemical engineering. However, the knowledge of physical and chemical processes of trace gaseous components, including radical species, on heterogeneous surfaces is limited.

Schwartz¹¹⁾ studied the transport process pertinent to the uptake of gases by liquid-water clouds in a comprehensive manner and indicated that information from laboratory studies was needed to understand interfacial mass transport. The overall process of the mass transport was considered as consisting of the following subprocesses: 1) mass transport of gases in the bulk gas phase to the aqueous surfaces (gas-phase diffusion), 2) interfacial mass transport, 3) hydration and possible acid-dissociation equilibria, 4) mass transport of dissolved species in the aqueous phase (aqueous-phase diffusion), 5) chemical reaction in the aqueous phase, 6) mass transport of reaction products in the aqueous phase, 7) possible evolution of volatile product species into the gas phase, and 8) subsequent mass transport of the evolved gaseous product.

Mass transport in the gas phase just above the interface (sub-process 2)) occurs by molecular diffusion. The flux into the aqueous phase is related to the gas-kinetic collisions on the surface by introducing the following parameters. The accommodation coefficient, α , is defined as the fraction of collisions of the gas-phase species with surface that results in dissolution. Another quantity, the

uptake coefficient, γ , is defined as the fraction of collisions that removes the species from the gas phase, corresponding to the net transport of species to the aqueous phase. The distinction between α and γ becomes important when desorption occurs. When a surface comes close to saturation, desorption occurs to larger extent, which reduces net uptake rate, and hence γ approaches zero. γ is the quantity actually measured in laboratory studies, and is the upper limit to α if it is measured without desorption. According to Schwartz¹¹⁾, for a γ value less than 10^{-2} , interfacial mass transport is more restrictive to the rate of overall process than gas-phase diffusion, and the dependence of the overall mass transfer rate is linear on γ at low γ values less than 10^{-3} .

So far, experimental data for γ of trace gaseous species on liquid surface are very limited. Recently, several groups^{2, 3, 9, 13, 14, 16)} have carried out measurements of γ for some species important in atmospheric chemistry. Experimental methods employed are; a droplet gas flow reactor method by Worsnop *et al.*¹⁶⁾, a similar technique for γ on H_2SO_4 aerosol by Fried *et al.*³⁾, a stopped-flow method by Tang and Lee¹³⁾, a wetted wall flow tube method by Utter *et al.*¹⁴⁾, a Knudsen cell flow reactor method for γ on ice surface by Quinlan *et al.*⁹⁾, and a newly designed bubble column reactor method by De Bruyn *et al.*²⁾.

Common to these studies is that the γ values are determined by macroscopic observations of average loss of the density in the bulk gas phase after contact with the liquid. Although each method is sophisticated enough to overcome experimental difficulties, some problems are still remaining. 1) Because of the average loss measurements, large errors are intrinsically included, particularly for small γ values. 2) These techniques are dependent on the assumed gas flow fields which are not so easy to determine actually.

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3) The reliability is very much affected by the estimation of the diffusion process, because gas-phase diffusion accounts for a large part of the overall loss process, particularly at small γ . At the same time, possible nonhomogeneous distribution of water vapor in the bulk gas phase makes it difficult to estimate the effective values of diffusion coefficients. 4) All the techniques except the droplet gas flow method have the inherent limitation that surface saturation or surface contamination may come to a serious level because of the relatively long contact time. 5) The technique utilizing a Knudsen cell is limited to surfaces under a very low pressure.

Our idea for direct observation is based on the concept that the concentration distribution of the species reflects the weight of individual sub-processes. In the bulk gas phase the mass flux of the species is mainly controlled by convective transport. On the contrary, molecular diffusive transport is dominant in the region near the surface that acts as a sink. If a direct and precise measurement of the concentration distribution is possible in this region, the determination of γ can be made with full accuracy.

The flow field that we have employed is an impinging flow field. The advantages of using it are mentioned below. 1) An impinging flow field where a vertical gas flow encounters a liquid flow coaxially from the opposed site is expected to give a steady flow adequate for observation. 2) The species in the gas phase always contact with the fresh aqueous surfaces at least on the central axis. 3) Treatment as an axi-symmetric problem is valid. Similar methods have a number of applications^{1, 4, 8, 10, 12}, particularly those focusing on the understanding of transport processes and chemical kinetics in the combustion study.

For the direct observation, laser-spectroscopic measurement has been employed. One reason is that this technique is an *in situ* measurement without perturbing the observation field. Another is that the spatial resolution is high enough to detect the local concentration distribution above the surface.

1. Theory and Simulation

1.1 Model

An impinging flow field above an aqueous surface is shown in **Fig. 1**. The concentration profiles of the objective species are obtained by solving a set of coupled nonlinear two-point boundary value problem. Our model assumes that; 1) the stagnation plane is identical to the aqueous surface, which is flat within a certain distance from the center of the water surface, 2) gas and liquid flows are inviscid and laminar, 3) the gas flow is saturated with water vapor pressure, 4) the objective species is dilute enough, and 5) temperature is constant everywhere.

Let the coordinates be cylindrical. The origin of the coordinates is taken on the center of the aqueous surface. The z axis is normal to the aqueous surface with the positive direction into the gas side. The r axis is taken along the surface. Being derived from the boundary layer theory, the

Fig. 1 Impinging flow field

governing equations for continuity, momentum and species can be written as follows without taking any chemical reaction into account. Nomenclatures obey usual manner, except when otherwise stated.

$$\frac{\partial(ur)}{\partial r} + \frac{\partial(vr)}{\partial z} = 0 \quad (1)$$

$$u \frac{\partial u}{\partial r} + v \frac{\partial u}{\partial z} = U \frac{\partial u}{\partial r} + v \frac{\partial^2 u}{\partial z^2} \quad (2)$$

$$u \frac{\partial C}{\partial r} + v \frac{\partial C}{\partial z} - D \frac{\partial^2 C}{\partial z^2} = 0 \quad (3)$$

The boundary conditions at the gas discharge ($z = l$) are given by

$$v = v_{g0} \quad (4)$$

$$C = C_0 \quad (5)$$

The flux into the aqueous phase at the surface ($z = 0$) is linked to the effective collision numbers on the surface in terms of gas-kinetic theory, i.e.,

$$v = 0 \quad (6)$$

$$D \frac{\partial C}{\partial z} = \frac{\gamma v_m C}{4} \quad (7)$$

where v_m is a molecular velocity. On the central axis ($r = 0$)

$$\frac{\partial C}{\partial r} = 0 \quad (8)$$

$$u = 0 \quad (9)$$

is obeyed. The free stream tangential and transverse

Fig. 2 Concentration profiles of SO_2 above surface in simulation for various γ values $C_0 = 8.29 \times 10^{13}$ molecule/cm³, $P = 11.9\text{kPa}$, $T = 293\text{K}$, $v_{g0} = 93.0\text{cm/s}$

velocities outside of the boundary layer are given as $U = ar$ and $V = -2az$, respectively, where a is a strain rate. Then the following functions are introduced.

$$u = \frac{r}{2} f'(z) \quad (10)$$

$$v = -f(z) \quad (11)$$

$$f(z) = 2\sqrt{av} \cdot \varphi(\xi), \quad \xi = \sqrt{\frac{a}{v}} z \quad (12)$$

, where $f(z)$ is named the boundary layer function and $\varphi(\xi)$, the stream function. Equations (1) and (2) can be transformed into an ordinary differential equation.

$$\varphi''' + 2\varphi\varphi'' - \varphi^2 + 1 = 0 \quad (13)$$

We first obtain the solution of Eq. (13) by Homann⁵⁾ and Howarth's method⁶⁾. Then, a finite difference method is applied to solving Eqs. (3) - (9) with upward differencing, by employing the value of $\varphi(\xi)$.

1.2 Simulation

In order to understand the effect of γ on the distributions of active species in the gas phase, we have treated the case of SO_2 . Simulation has been conducted assuming γ values for SO_2 from 1 through 10^{-6} under the same conditions as the experiments which will be described later, i.e., total pressure, P , 4.00 - 11.97kPa; temperature, T , 275.85 - 303.25K (corresponding to 0.745 - 4.27kPa of saturated water vapor); and the gas flow velocity at the discharge v_{g0} , 32.5 - 720.0cm/s. The diffusion coefficient, D , is taken to be equal to that of SO_2 calculated from the approximate method by Wilke¹⁵⁾, employing the data of binary diffusion coefficient for SO_2 in He and in gaseous H_2O reported by Marrero and Mason⁷⁾.

Examples of the simulated spatial distributions are shown in **Fig. 2**. The concentration distribution of the

Fig. 3 Observation vessel

species above the surface can be approximated to be linear in the region up to a height of 2 or 3 mm from the surface. This fact indicates that we can determine the γ value from the slope of the profile and the intercept at the ordinate (surface concentration) by using Eq. (7), if the distribution profile was determined experimentally. By determining the γ values from the simulated distributions in terms of Eq. (7) and comparing these values with the values assumed in the simulation calculation, possible errors in the above procedure have been estimated. All over the range of conditions employed, it has been ascertained that the estimation of γ by using the distribution profile in the region of 0 - 2 mm height produces errors within -20% (- means that the estimated γ is smaller than the true γ). The accuracy is much more satisfactory (errors within -2%) for the γ ranging from 10^{-2} through 10^{-5} .

The requirement of the spatial resolution to obtain the local concentration of the objective species is 0.1 mm in the vertical direction according to the above consideration.

2. Experimental

2.1 Impinging flow field and observation vessel

An impinging flow apparatus designed for direct observation of concentration profiles of trace species above a surface is shown in **Fig. 3**. The gaseous flow including a small amount of objective species is discharged from the upper vertical pipe of 1/2 inch o.d. (10.5mm i.d.), and then collides with the aqueous surface. The liquid, a pH adjusted doubly-distilled water, is flowed coaxially to the upward direction from the lower pipe of the same size. The above opposed pipes-system is settled in a double-cylinder vessel made of SUS 316. The temperature in the vessel is controlled by flowing a thermoregulating fluid between the inner and outer cylinder walls. The inner cylinder is 198.0 mm high and 66.0 mm in diameter, which is large enough to avoid wall effect and disturbance of the flow. The opposing two discharge pipes are placed in the center of the cylinder at 24.95 mm distance from each other. The distance between the aqueous surface and the gas discharge position is 20.05 mm in typical experiments.

Fig. 4 Experimental setup

The pipe edges are shaped slightly bell-mouthed to guarantee ideal streamlines. The flow guide surrounding the lower pipe is needed in order to drain the aqueous flow smoothly and to protect the windows from coverage by the splash.

The quartz windows for incidence and transmission of the laser beam were fixed with flanges at the Brewster's angle. Two longitudinal slits of 2.4 mm width are positioned inside of the vessel at the inlet and outlet window for the laser beam in order to minimize scattered light.

2.2 Experimental setup

Figure 4 illustrates the total system. The vessel was kept at a given reduced pressure (P , 3.5 - 12.1 kPa) by a rotary pump. The objective gases, such as SO_2 diluted in He and humidified He, were supplied through the individual mass flow controller. The ratio of the former gas flow rate to the latter was kept at less than 0.17. The inlet lines were maintained at the same temperature as the observation vessel. Thus the partial pressure of the water vapor was expected to be almost uniform above the surface. The temperature-controlled water was supplied to the discharge pipe by a magnet pump with no pulsation, and flow was monitored by a flow sensor. The drained water was collected in a receiver tank, whose inlet was positioned always below the surface of the collected water. Liquid circulation directly back to the water reservoir without passing through the vessel was necessary to remove bubbles in the water line, because bubble evolution badly affected the interference with measurements. The water reservoirs were kept at the pressure balanced within $\pm 7\text{Pa}$ to that of the observation vessel by controlling the flow of He by a piezo valve.

2.3 Experimental procedure and laser induced fluorescence measurements

The experiments for SO_2 were performed for demonstration of the applicability of the proposed method. To realize a direct measurement, a technique of laser induced fluorescence spectroscopy was utilized whose spatial resolution was intrinsically high. The spatial distribution of SO_2 concentration was determined by measuring the intensity of the laser induced fluorescence excited at 224.34 nm, which corresponded to the head of the (112) - (000) band of the $\tilde{C} - \tilde{X}$ transition.

A dye laser beam pumped by a XeCl excimer laser (Lambda Physik FL3002 / LPX 100) was frequency-

Fig. 5 Detection optics system

a: aperture, b: black box, c1, c2: collection lens, ft: filter, p: photomultiplier

doubled by a BBO crystal and focused at the position to be monitored in the observation vessel using a quartz lens ($f = 200\text{ mm}$). The diameter of the laser beam at the beam waist was measured to be less than 0.10 mm. Both the incident and the transmitted laser light were monitored by photodiodes. The laser beam was adjusted horizontally within 0.01° with a set of phase-sensitive detectors.

Fluorescence was detected at right angles to the incident beam by a photomultiplier equipped with a fast preamplifier, using the detection optics system illustrated in Fig. 5. The detection optics were set as follows: the central axes of two collection lenses ($f = 50\text{ mm}$) were adjusted so as to collect emission from a single point; Apertures of 0.3 mm i.d. were placed at distances of $2f$ from the individual lens; to minimize the scattered light from the surface or the window and to limit the solid angle, the lower half and the center part (within 1.3 mm from the axis) of the collection lens (c1) which is placed near the observation vessel were blocked, and the center part (within 1.0 mm from the axis) of the other lens (c2) was blocked; two pieces of glass filter transmitting 260 - 400 nm were also placed in the light pass; all the optics were set on an optical bench and covered in a black box. Both the detection optics system and the observation vessel were placed on individual XYZ-stages adjustable with 0.05 mm accuracy.

The spatial resolution in the vertical and depth directions was dependent on the radius of the laser beam; and the resolution in the horizontal direction was dependent on aperture diameter. Thus, the estimated resolutions were 0.1 mm, 0.1 mm and 0.3 mm, respectively.

The detected signals were transmitted to a boxcar averager (PAR 4121B) or a digital oscilloscope (Lecroy LS140), and the treated signals were transferred to a personal computer through an AD converter.

The position of the aqueous surface was determined by searching for the position where the signal intensity of the transmitted laser light through the observation vessel decreased to half of its original value.

In the experiments, the linear velocity at the center of the pipes of gas and water were adopted for v_{g0} and v_{a0} , individually, assuming a Poiseuille flow. All the experiments were performed under laminar flow conditions.

Fig. 6 Excitation spectra of SO_2 in $\tilde{\text{C}} - \tilde{\text{X}}$ transition observed at two different heights above water surface
 $C_0 = 7.92 \times 10^{13}$ molecule/ cm^3 , $P = 12.0$ kPa,
 $T = 294$ K, $v_{g0} = 92.7$ cm/s, $v_{a0} = 2.3$ cm/s,
pH of water = 5.6

Fig. 7 Calibration curve for SO_2 concentration in presence of water vapor partial pressure of water = 2.34 kPa,
 $P = 12.0$ kPa, $T = 293$ K

3. Results and Discussion

3.1 Reliability of the measurements of SO_2 concentration distribution

Figure 6 shows the excitation spectra of SO_2 in the $\tilde{\text{C}} - \tilde{\text{X}}$ transition measured at different heights along the z axis using water of pH = 5.6. The upper spectrum was obtained at 17.3 mm height above the surface and the lower one at 0.2 mm above the surface. The profiles of the vibronic bands are the same. Thus SO_2 itself is monitored by the laser-spectroscopic technique independent of height of the measurement.

An example of the calibration curve for SO_2 concentration is shown in Fig. 7, where the partial pressure of water vapor is 2.34 kPa and the input laser energy is 0.26 mJ/pulse. The fluorescence intensity is linear against the concentration of SO_2 over the entire concentration range of $3.3 \times 10^{11} - 1.7 \times 10^{14}$ molecules/ cm^3 . The dependence on the laser energy was also examined to be linear from 0.031 mJ/pulse through 0.48 mJ/pulse. Hence quantitative analysis is proved to be feasible in the presence of water vapor.

Assuming the case that water vapor is distributed nonuniformly and noting that it is difficult to detect local concentration of water vapor, the quenching effect of H_2O on the fluorescence intensity should be paid attention. There have been, however, no reliable quenching data of H_2O for

Fig. 8 Observed fluorescence intensity along z axis under surface saturated condition
 $C_0 = 8.12 \times 10^{13}$ molecule/ cm^3 , $P = 11.7$ kPa,
 $T = 293$ K, $v_{g0} = 91.9$ cm/s, $v_{a0} = 0$ cm/s, pH of water = 3.0

SO_2 in its $\tilde{\text{C}}$ state. Hence another approach is necessary. As shown in Fig. 2, when the γ value is below 10^{-5} , the concentration distribution is flat. Worsnop *et al.*¹⁶⁾ reported that the surface became saturated readily when the water was acidic. The effect of the surface saturation reduces the γ value to almost zero, which should lead to a flat profile. Accordingly, the fluorescence intensity which is obtained under conditions of surface saturation should be constant everywhere along z axis, if it is not affected by the quenching effect of H_2O . Figure 8 shows an experimental result obtained under the condition that water adjusted at pH 3.0 was kept stationary long enough for surface saturation with the gas flowing. Obviously the profile in Fig. 8 is flat, which verifies that water vapor is distributed uniformly above the surface, or if it is distributed nonuniformly, the effect of quenching is negligibly small. In other words, the observed profile is not affected by the nonhomogeneous distribution of water vapor even if the nonhomogeneity exists. In the case when water is flowing, the situation is the same with respect to the quenching effect of water vapor.

As a whole, it is concluded that the SO_2 concentration can be measured accurately by the present fluorescence detection technique.

3.2 Determination of γ values and their dependence on the flow condition in the gas phase

As one example, an experimental distribution of SO_2 concentration above the water surface obtained under a typical condition using water of pH 13.0 is compared with the simulated distributions in Fig. 9. The alkaline condition of the supplied water was adopted because the γ value was less affected by acid-dissociation equilibria at higher pH than 10.²⁾ The data in the region below the point of 0.15 mm above the surface were excluded because they were affected by the scattered light from the surface. It is seen that the measured distribution is linear in the region close to the surface and thus γ can be determined readily by means of Eq. (7).

The diffusion coefficient, D , was estimated as described in the simulation part. The obtained γ was 0.028

Fig. 9 Simulated and experimental distribution curves of SO_2 on the water surface
 $C_0 = 8.29 \times 10^{13}$ molecule/cm³, $P = 12.0$ kPa,
 $T = 293$ K, $v_{g0} = 93.0$ cm/s, $v_{a0} = 5.9$ cm/s,
 pH of water = 13.0

Fig. 10 Effect of gas flow velocity on γ values
 $C_0 = 4.34 \times 10^{13}$ molecule/cm³, $P = 12.0$ kPa,
 $T = 293$ K, $v_{a0} = 2.1$ cm/s, pH of water = 13.2

from the profile in Fig. 9. The possible errors involved in this case were estimated as follows. Determination of SO_2 concentration itself was repeatable within 0.5%. It led to a maximum error of 5% in the calculation of the slope by Eq.(7). The spatial resolution of the detection along the axis was 0.1 mm. The mechanical positioning of the observation vessel was accurate within ± 0.05 mm. The determination of the position of the surface was influenced within ± 0.1 mm by the inconsistency caused by the bubbles mixed in the water flow. Considering the above-mentioned factors, the maximum uncertainty which was involved in the determination of the height of the observation point was ± 0.25 mm. This corresponded to an error of 30% in the estimation of the concentration of SO_2 at the surface. Taking into consideration the previous 5% error altogether, the total error was estimated to be within 35%. For lower γ , the errors are expected to be much smaller.

The effect of the gas flow velocity, v_{g0} , on γ ranging from 35 cm/s to 730 cm/s is shown in Fig. 10. The γ value is independent of the gas flow velocity over the entire range studied, which guarantees that Eq.(7) is valid and independent of the momentum flow in the outer region.

Figure 11 shows the results for the total pressure, P , ranging from 3.5 kPa to 12.1 kPa. The diffusion coefficient

Fig. 11 Effect of total pressure on γ values
 $C_0 = 7.81 \times 10^{13}$ molecule/cm³, $T = 293$ K,
 $v_{g0} = 91.9$ cm/s, $v_{a0} = 2.2$ cm/s, pH of water = 13.2

changes from 4.46 cm²/s to 2.39 cm²/s, being dependent on the total pressure. The deviations of γ obtained in the lower pressure range are considered to be caused by bubble mixing in the water which results in the inconsistency of the water surface. The perfect removal of dissolved gas in the water was not actually attained, so the decrease of the total pressure was accompanied by an increase of bubble evolution. It is concluded, except for the lower pressure range, that the variance in the total pressure and the resultant variance in the diffusion coefficient does not affect the γ value.

Worsnop *et al.*¹⁶⁾ reported 0.11 for γ under comparable conditions (pH of water = 13.2, $T = 293$ K) to the present experiments. The present result is of a similar order, which is satisfactory, if one considers the difficulty in determination of uptake coefficients.

Conclusion

The principle, analysis and experimental setup for determining uptake coefficient by direct observation were described. The transport of SO_2 from gas phase flow which was colliding with an aqueous surface was investigated as an example in order to verify the validity of the proposed method. The concentration gradient according to interfacial mass transport was actually observed and the obtained results verified the validity of the proposed method. The determination of γ by this method is not affected by the limitation of gas-phase diffusion or the flow condition in the gas phase. The present method is, thus, demonstrated to be applicable to determination of the uptake coefficient. This method has the merit of direct determination of γ , and is not affected by gas-phase processes, compared with previous methods which needed the assumption of no effective limitation of the gas-phase diffusion. For the interpretation of the meaning of γ , however, further work taking into account the complex chemistry in the aqueous phase is needed.

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Nomenclature

a	= strain rate	[s ⁻¹]
C	= concentration of objective species	[molecule/cm ³]
C_0	= concentration of objective species at the discharge	[molecule/cm ³]
D	= diffusion coefficient of objective species in gas phase	[cm ² /s]
f	= focal length of a lens	[mm]
$f(z)$	= boundary layer function	
r	= coordinate along the surface	[cm]
u	= velocity component in r direction	[cm/s]
U	= free stream tangential velocity outside of boundary layer	[cm ² /s]
v	= velocity component in z direction	[cm/s]
V	= free stream transverse velocity outside of boundary layer	[cm ² /s]
v_{a0}	= linear velocity of liquid flow at center of water discharge	[cm/s]
v_{g0}	= linear velocity of gas flow at center of gas discharge	[cm/s]
v_m	= molecular velocity of objective species	[cm/s]
z	= coordinate normal to surface	[cm]
α	= accommodation coefficient	[-]
γ	= uptake coefficient	[-]
ν	= kinematic viscosity	[cm ² /s]
ξ	= non-dimensional variable	
ϕ	= stream function	

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