A unique dosing system for the production of OH under high vacuum for the study of environmental heterogeneous reactions

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A unique dosing system for the production of hydroxyl radicals under high vacuum for the study of environmental heterogeneous reactions is described. Hydroxyl radicals are produced by the photodissociation of a hydrogen peroxide aqueous gas mixture with 254 nm radiation according to the reaction \( \text{H}_2\text{O}_2 + h\nu \rightarrow \text{OH} + \text{OH} \). Under the conditions of the current design, 0.6% conversion of hydrogen peroxide is expected yielding a hydroxyl number density on the order of \( 10^{10} \) molecules/cm\(^3\). The flux distribution of the dosing system is calculated using a Monte Carlo simulation method and compared with the experimentally determined results. The performance of this unique hydroxyl dosing system is demonstrated for the heterogeneous reaction with a solid surface of potassium iodide. Coupling of the hydroxyl radical dosing system to a quantitative surface analysis system should help provide molecular level insight into detailed reaction mechanisms. © 2008 American Institute of Physics. [DOI: 10.1063/1.2839915]

I. INTRODUCTION

The importance of heterogeneous chemistry within the atmosphere has been firmly established in the literature for decades\(^1\) and has become the focus of many research groups. Gas-solid and gas-liquid heterogeneous processes have been recognized as key players in relation to the Antarctic/Antarctic ozone depletion,\(^2,3\) global stratospheric ozone loss,\(^4\) and oxidation of organic carbon matter in the troposphere\(^5-8\) (see reviews by Rossi,\(^9\) Finlayson-Pitts,\(^10\) and Molina et al.\(^11\) for a comprehensive discussion of relevant heterogeneous processes throughout the atmosphere).

The hydroxyl radical is a key component of the atmosphere for its high oxidizing potential that transforms many trace components into water-soluble forms that are removed from the atmosphere through a variety of routes.\(^1,12,13\) Uptake coefficients for OH on many surfaces of atmospheric relevance have resulted in conflicting results (a scan of the literature reveals uptake coefficients that span orders of magnitude for the same reaction) often due to the inherent complexity of studying multiphase systems.\(^14-22\) The large range of uptake coefficients have greatly limited our understanding of reaction mechanisms on a molecular level and have revealed the need for more fundamental studies of many heterogeneous processes. Laux et al.\(^23,24\) were able to show how ultrahigh vacuum (UHV) quantitative surface characterization using x-ray photoemission spectroscopy (XPS) and transmission electron microscopy of the uptake of nitric acid on solid surfaces of sodium chloride could provide insight into detailed reaction mechanisms at a fundamental level.

However, in spite of the above-mentioned success, most of the data on heterogeneous reactions has been obtained using more traditional experimental uptake methods such as Knudsen cells,\(^25-28\) flow tube studies,\(^29\) falling-droplet apparatus,\(^30,31\) bubble apparatus,\(^32\) and aerosol chambers.\(^33-36\) The advantage of coupling uptake measurements with quantitative UHV characterization is that in addition to the surface uptake coefficient, surface elemental composition can be determined from core-level peak intensities (XPS), and in many cases, information about chemical bonding can be obtained from core-level peak shifts or from valence-band photoemission spectroscopy.

Herein, we present the design and development of a unique dosing system for the production of OH radicals under high vacuum coupled with XPS for the quantitative study of heterogeneous surface reactions. The design of the OH dosing system, including a detailed description of the components is discussed, followed by a thorough analysis of the flux distribution emitted from the doser. An example of the application of this dosing system, the reaction of hydroxyl with a solid potassium iodide single crystal surface is presented.

II. DESIGN

Our design of a high vacuum hydroxyl radical doser produces hydroxyl radicals by photodissociation of a \( \text{H}_2\text{O}_2 / \text{H}_2\text{O} \) gas mixture at 254 nm (details of the radical production are covered in the following section). Conceptually, the doser consists of a central dosing tube through which a \( \text{H}_2\text{O}_2 / \text{H}_2\text{O} \) mixture flows. The central dosing tube is concentrically surrounded by ten mercury pen ray lamps that provide the 254 nm radiation for photodissociation. The components of the dosing system are shown in Fig. 1; a linear translator (A), the central dosing tube (B), a sapphire seal leak valve (C), a high pressure hydrogen peroxide aqueous cell equipped with a baratron pressure transducer (D), a six-
A detailed description of the dosing tube, the other components of the dosing system and their respective roles in the production of hydroxyl radicals follow.

A. Dosing tube

A schematic drawing of the hydroxyl radical dosing tube is presented in Fig. 2. The doser consists of a type 214 quartz dosing tube with an inner diameter of 20.0 mm and an outer diameter of 22.0 mm housed in a water jacket of the same material. Type 214 quartz is used as it provides the highest transmission to 254 nm radiation (90.8%) thereby providing the greatest flux to the gas sample. The water jacket allows chilled water to flow through the system and prevent both the increase in the gas temperature of the H₂O₂/H₂O mixture and the solid sample surface of interest. A graded glass seal provides the transition from the type 214 quartz tubing to a small welded bellows at the top of the dosing tube that is, in turn, connected to a 1.33 in. CF vacuum flange. The small welded bellows at the top of the dosing tube provide a limited amount of flexibility to forces that may be applied to the dosing tube during setup and installation onto the vacuum system. A bored through 4.5 in. CF vacuum flange makes the connection to the vacuum system. A metal tube, electron beam welded to ensure vacuum compatibility (63.5 mm outside diameter) extends from the vacuum flange to which two metal spacers have been welded. The two metal spacers are multifunctional. They provide a placeholder for the mercury pen ray lamps and the water cooling inlet line, while also providing two small holes so that the mercury pen ray lamp section can be purged with nitrogen gas (certain mercury pen ray lamps are known for producing ozone in oxygen containing environments). A graded metal-to-glass seal at the end of the metal tube provides the transition needed to seal to the end of the dosing tube. It should be noted that the graded metal-to-glass seal (stainless steel to quartz) requires a finite length (∼4–6 in.) and thereby limits the dimensions of this design.

A schematic showing the details of the hydroxyl radical generation area is shown in Fig. 3. It is shown in cross section for clarity. Six metal rods extend from the top of the vacuum flange ~9 in. making the inside components accessible and allowing for the mercury pen ray lamps to be removed if needed. The metal rods provide support for the components that are attached at the top of the dosing tube (see Fig. 1). The inset of Fig. 3 shows the ten mercury pen ray lamps that surround the dosing tube. Metal spacers (as described above) provide a means to position the lamps in as close proximity around the dosing tube as possible. The lamps are 22 mm from the center axis of the dosing tube. In the current design, light emitted from an angle of 54° intercepts the central dosing tube. As such, 15% of the emitted light from each lamp contributes to the photodissociation of hydrogen peroxide.

B. Vacuum components

The dosing tube is mounted to a 100 mm linear translator (VGScienta ZLTS0410) that permits the height of the dosing tube to be varied inside the vacuum chamber (to be discussed in the flux calibration section). Ten mercury pen
ray lamps (UVP, 90-0004-11) 152.4 mm in length each provide 4.250 mW of total intensity at 254 nm \(^{39}\) with 637.5 \(\mu\) W per lamp intercepting the central dosing tube. A turbomolecular pump (Leybold TurboVAC 50) provides pumping through a bypass valve that regulates the pressure of the \(\text{H}_2\text{O}_2\) vapor mixture in a six-way cross, mounted directly above the dosing tube. Pressure inside this cross is monitored with a baratron pressure transducer. Random processes associated with the production of hydroxyl radicals including reactions such as \(\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2\) are eliminated in the current design as the irradiation region of the dosing tube is in the free molecular flow regime where molecule-molecule collisions are not expected to occur. With the current doser design, samples are limited to ones that exhibit no background reactivity with the \(\text{H}_2\text{O}_2/\text{H}_2\text{O}\) gas mixture.

### III. FLUX CALIBRATION

#### A. Theoretical approach

Monte Carlo (MC) simulation methods were used to determine the profile of the gas flux emitted by the dosing system. Random gas effusion was assumed with an isotropic velocity distribution in the injection area of the doser. The MC simulation assumes free molecular flow throughout the dosing tube and thus uses a single molecule approach where the time scale is arbitrary. Whenever a molecule collides with the inner wall of the dosing tube, it is scattered in a random angle having a cosine distribution (provided that the velocity distribution in the injection area of the doser). The cross section for photodissociation of hydrogen peroxide at 254 nm is well known to be \(6.7 \times 10^{-20}\) cm\(^2\)/molecule. \(^22\) Hydrogen peroxide 50% w/w in aqueous solution can be further concentrated by bubbling dry argon through the mixture if there is a desire to minimize the water content in the experiment. In the experiments described here, the hydrogen peroxide solution is used as provided. The \(\text{H}_2\text{O}_2/\text{H}_2\text{O}\) mixture is passed through the dosing tube from a region of high pressure (the pressure backing the dosing tube can be varied from \(2 \times 10^{-5}\) to \(2 \times 10^{-2}\) Torr in order to vary the partial pressure of \(\text{H}_2\text{O}_2\) with our current baratron pressure transducer) toward the ultrahigh vacuum chamber where the solid sample is kept. In the current design, the interaction region with 254 nm radiation is 152.4 mm (the length of the mercury pen ray lamps) resulting in an average hydrogen peroxide resonance time of 0.36 ms in the irradiation area. Corrected for the irradiation angle of 54° that intercepts the central dosing tube the total intensity at 254 nm is \(8.145 \times 10^{15}\) photons/s for the ten lamps employed in the current design. The Beer-Lambert law,

\[
I = I_0 e^{-\sigma \rho \ell}
\]

is used to calculate the theoretical conversion of hydrogen peroxide into hydroxyl radicals according to the reaction of Eq. (1) with a product quantum yield of 2.1 \(\sigma\) is the cross section for photodissociation at 254 nm \((6.7 \times 10^{-20}\) cm\(^2\)/molecule). \(^22\) \(\rho\) is the number density of hydrogen peroxide (typical values are in the range of \(5 \times 10^{12} - 5 \times 10^{13}\) molecules/cm\(^3\)), and \(\ell\) is the path length (2.0 cm). \(I_0\) is the intensity of the ten mercury pen ray lamps \((8.145 \times 10^{15}\) photons/s) incident on the central dosing tube and \(I\) is the intensity of the transmitted light. It is assumed in this calculation that there is a linear pressure drop across the dosing tube from the region of high pressure behind the dosing tube to the sample surface. The current doser design has a conversion rate of 0.6%.

Hydroxyl radicals are generated in the molecular flow regime of our high vacuum compatible dosing system by the following photoreaction,

\[
\text{H}_2\text{O}_2 + h\nu(254\text{ nm}) \rightarrow \text{OH} + \text{OH}.
\]
atomically rough glass surface is not expected to preferentially scatter the gas molecules in any one direction. The trajectory of each particle is followed until it either leaves the dosing tube through its exit or is backscattered to the injection area. A data set with an angular distribution of relative gas flux intensity is obtained by summing all particles leaving the dosing tube within a specific polar angle interval, integrated over the whole azimuth. In addition, sets of virtual planes are placed at different distances in front of the dosing tube exit, perpendicular to the tube axis. For each exiting molecule, coordinates for which the particle intersects the given planes are calculated. Intersection points can be then summed over small square units, generating the flux density profile.

Figs. 4(a) and 4(b) present the relative incident flux intensity for a sample-to-doser distance of 2 and 12 mm, respectively. In Fig. 5, the relative flux profiles for sample-to-doser distances of 2–20 mm in 2 mm increments are compared. Generally, it can be seen that with increasing sample-to-doser distance, the flux distribution in the main gas stream decreases while the background (distribution tail) increases as the effusive beam diverges down stream. On the other hand, the further the plane from the end of the dosing tube, the more uniform is the main part of the flux profile. This should be taken into account in situations when homogeneous exposure is desired. As an example, for a typical sample size of 10 mm², the variation of incident beam flux is only 10% if the sample-to-doser distance is 12 mm.

B. Experimental approach

In order to verify the validity of our theoretical approach, a simple beam monitor based on the principle of an accumulation detector was set up to measure the experimental flux density. The measurement of the pressure inside the detector is provided by a high accuracy extended range ion gauge (Granville-Phillips 370 Stabil-ion). The detector itself is a 9 mm inside diameter stainless steel tube which is welded to a 2.75 in. CF double-sided vacuum flange and fully coated with gold (0.2 µm thick layer) to reduce gas adsorption. Near the front end of the tube, there is a 350 µm diameter hole chamfered 45° at its inner side to form a very thin entrance aperture to the detector volume. Both the tube and the ion gauge are mounted on an xyz manipulator that allows probing an effective area of 40 × 25 mm². For nonadsorbing gases such as argon (which was used in this calibration), the response time of the beam monitor needed to establish an equilibrium pressure depends on the aperture area and the detector volume. This was approximately 45 s. There is a drop in pressure of two orders of magnitude across the length of the dosing tube from the region of high pressure backing the doser to the sample surface. The pressure of the main chamber remained one order of magnitude lower than the pressure at the sample surface (however, the pressure of the main chamber is a function of total pumping speed). The pressures measured with the ion gauge can be directly converted to absolute flux using the Langmuir-Hertz equation (also called the Knudsen-Hertz equation) which analytically describes the frequency of collisions \( Q \) of an ideal gas with a surface,

\[
Q = \frac{P}{2\pi mk_BT},
\]

where \( Q \) is the flux in molecules/s and \( P \) is the pressure inside the beam monitor following a correction of the background pressure.\(^{41,42}\)

The experimentally obtained gas beam flux profile is presented in Fig. 6. The data are presented as a relative flux at the sample surface where the pressure of the injection area is set to one \( (Q_0) \). When compared with the results of the
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The photoemission lines of I/H20849 of the doser design. Solid potassium iodide samples were prepared ex situ by cleavage of a single crystal along the (100) plane. Immediately following cleavage, the samples were transferred into the vacuum chamber. Figure 8 shows the photoemission spectrum of this solid surface. The photoemission lines of I (4d), K (2p), K (2s), I (3d), and the Auger line of I(MNN) are present in order of increasing binding energy. This sample is completely devoid of adsorbed water as seen by the absence of O (1s) photoemission intensity (~531–533 eV).

The results that follow are representative of a 5.0 mTorr backing pressure of the H2O2/H2O mixture and a sample-to-doser distance of 2 mm. Under these experimental conditions, dosing the sample with the H2O2/H2O mixture while the mercury pen ray lamps are turned off results in no net uptake in the O (1s) region of the photoelectron spectra even after a prolonged exposure of 90 min. Figure 9 shows high resolution photoelectron spectra of the K (2p) and O (1s) regions of a freshly cleaved single crystal KI (100) surface and the resulting changes following an exposure of 30 min to the dosing system with the mercury pen ray lamps turned on, producing hydroxyl radicals at 0.6% conversion. A large uptake in the O (1s) region resulting from the build up of hydroxyl on the sample surface is clearly seen.

Varying several parameters can regulate the exposure of hydroxyl to the surface. The concentration of peroxide in solution can be either increased (to produce more hydroxyl) or decreased (to produce less hydroxyl), the flux of the mercury pen ray lamps can be adjusted by varying the number of lamps that are turned on during the dosing process. Also, the hydroxyl-sample dosing time can be controlled. Figure 10 shows hydroxyl uptake on the surface of solid potassium iodide (100) as a function of exposure time. The data are presented as a ratio of the O (1s) peak intensity to the K (2p) peak intensity. An increase in O (1s) peak intensity is ob-

**FIG. 8.** Survey spectra of a freshly cleaved solid sample of potassium iodide (100). Photoemission lines for I (4d), K (2p), K (2s), and I (3d) as well as the Auger line I (MNN) are observed. Note that there is no intensity in the region of the spectra corresponding to I (1s) (~531–533 eV).

**FIG. 9.** (Color online) High-resolution photoemission spectra of the K (2p) and O (1s) regions from a solid sample of KI (100) before (shown in red) and after (shown in blue) a 30 min exposure to the hydroxyl radical dosing system. A large uptake in O (1s) is observed. No increase in O (1s) photoemission intensity occurs during a similar exposure with the mercury pen ray lamps turned off. Small intensity from adventitious carbon is seen at 285 eV before and after dosing.
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1 B. J. Finlayson-Pitts and J. N. Pitts, Jr., Chemistry of the Upper and Lower Atmosphere (Academic, New York, 2000).