Abstract. The hydroxyl radical (OH) is the most important oxidant in the atmosphere and plays a central role in tropospheric chemistry. Ambient OH is extremely difficult to measure because of its low concentration and high reactivity. We have developed and optimized a chemical ionization mass spectrometry (CIMS) system to measure OH based on ion-assisted mass spectrometry. A calibration unit was developed based on chemical actinometry to convert detected signals to OH concentration. Different types of ion sources (^{210}Po and corona source) and scavenger gases (propane and C_3F_6) were compared. Radioactive ion source (^{210}Po foils) was chosen for lower detection limits, and propane was selected for high elimination efficiency and the negligible influence on the signal stability. The sensitivity of the CIMS instrument to OH radicals is influenced by the efficiencies of conversion reaction, ion conversion, and ion transmission. Through optimizing their efficiencies by changing the flow rates and electric fields, an optimal sensitivity was determined for our system. The background noise from OH interferences was reduced by adjusting the flow rate of scavenger gas. The CIMS system achieved a detection limit of ~0.15 $\times 10^6$ molecules cm^{-3} (signal/noise=2). The CIMS was then taken out to measure ambient OH at an urban site in Hong Kong in April 2019. An obvious diurnal pattern of OH radicals was observed, with the highest concentration of ~6×10^6 molecules cm^{-3} at midday and the lowest concentration of ~0.25×10^6 molecules cm^{-3} at night, with an overall accuracy of about ±51%. The results demonstrated the capability of our CIMS for OH measurements on clear days. The tests and results from our study provide a useful reference to other researchers who wish to develop and apply the CIMS technique to measure OH and other chemicals.

1. Introduction

The hydroxyl radical (OH) is the most important atmospheric cleansing agent, and is responsible for the degradation and removal of most of trace gases (Crosley, 1997). In regions strongly affected by anthropogenic activities, reactions of OH with volatile organic compounds (VOCs) and carbon monoxide (CO) lead to the formation of organic peroxy (RO_2) and hydroperoxyl (HO_2) radicals. They react with NO to form nitrogen dioxide (NO_2), producing ozone (O_3) (e.g., Hofzumahaus et al., 2009). The reactions of OH with NO_2 and sulfur dioxide (SO_2) and the self- and cross-reactions of RO_2 and HO_2 transform the primary pollutants into low-vapor pressure gas molecules such as nitric acid (HNO_3), sulfuric acid (H_2SO_4), and highly oxidized organic molecules (HOMs) (Lu et al., 2012). In addition, the reaction with OH is the main removal pathway of methane, which is the third most important greenhouse gas according to the IPCC report (Stocker et al., 2013). Therefore, OH plays key roles in major environmental issues such as photochemical pollution, acid rain, haze, and climate change (Kulmala et al., 2004; Wang et al., 2017; Calvert et al., 1985; Lu et al., 2019).

The importance of OH in tropospheric chemistry was first recognized by Levy (1971). Since then, concerted efforts have been made to develop techniques to measure OH in the atmosphere (Heard and Pilling, 2003). However, the low concentration, high reactivity, and short lifetime (<1 s) of OH make it very difficult to be detected and quantified. The low concentration requires high sensitivities and small interferences in the instruments; the high reactivity demands a small loss in the sampling system, and the short lifetime requires measurement at a high temporal-spatial resolution. It is a big challenge to meet all of these requirements by a measurement system (Lu et al., 2019).

During the past decades, three major techniques have been developed for in-situ OH measurements: differential optical absorption spectroscopy (DOAS) (Wennberg et al., 1990), laser-induced fluorescence (LIF) (Perner et al., 1976), and chemical ionization mass spectrometry (CIMS) (Eisele and Tanner, 1991). DOAS and LIF techniques directly measure OH based on spectroscopic methods. The major advantage of DOAS is that it is self-calibrating via the well-known Beer-Lambert law, and thus does not require to separate a calibration device (Heard and Pilling, 2003). DOAS often serves as a primary standard for comparisons with other measurement techniques. However, the application of DOAS to the measurement of ambient OH is limited due to the interferences from other atmospheric constituents (Heard and Pilling, 2003). LIF measures OH by using pulsed 308 nm single photon excitation of OH at

low pressure with temporally delayed detection of the OH resonant fluorescence (known as fluorescence assay by gas expansion, FAGE) (Holland et al., 1995), and it requires calibration. The LIF technique has the advantages of direct excitation of OH and good selectivity and sensitivity (Heard and Pilling, 2003). Unlike DOAS and LIF, the CIMS technique measures OH indirectly based on an ion-assisted mass spectrometry method. It employs a chemical reaction scheme that OH is firstly converted into H_2SO_4 and subsequently measured by a specific chem-ionization method (Eisele and Tanner, 1991). CIMS has fewer interference and higher sensitivity compared to either DOAS or LIF techniques for OH measurement because of the higher collection efficiency of ions than photons (Heard and Pilling, 2003). As a result, CIMS processes the lowest detection limit for ambient OH measurement among the three techniques (Heard and Pilling, 2003).

LIF has been the most widely used technique for OH measurement in laboratory and field studies (Stone et al., 2012). However, some LIF instruments may suffer from interferences in environments of rich VOCs and poor NOx. Previous field measurements by LIF in forested regions have observed OH concentrations that are three to five times higher than those predicted by models with presently known OH sources and sinks (McKeen et al., 1997; Lelieveld et al. 2008; Hofzumahaus et al., 2009; Whalley 2011; Lu et al. 2012; Mao et al. 2012; Novelli et al. 2014; Feiner et al. 2016; Tan et al. 2017). The discrepancy was first attributed to the existence of an unknown source of OH in VOC-rich environment (Peeters et al., 2009; Hofzumahaus et al., 2009), whereas later studies found positive artifacts in some LIF instruments in such environments (Mao et al. 2012; Novelli et al. 2014; Feiner et al. 2016; Liu et al. 2018). For example, Mao et al. (2012) attributed 40-60% observed OH signal at a California forest to an interference in their LIF by using a chemical method to remove the interference. Recently, Liu et al. (2018) inferred the equivalent OH concentrations from measurements of isoprene and its oxidation products over Amazon, and found that the inferred OH concentrations compared well with the simulated results. On the other hand**,** other groups did not find evidence of the positive bias in their LIF systems, which have different design and configurations, continued to attribute the model underestimated OH to the presence of OH unknown source(s) at their study sites (Whalley 2011; Stone et al., 2012; Fuchs et al.2012; Lu et al. 2012; Tan et al. 2017). It is highly desirable to deploy an alternative technique to re-examine the OH issue in forested regions.

The CIMS technique for measuring OH was first developed at Georgia Institute of Technology by Eisele and Tanner (1991). The system was further improved at National Center for

Atmospheric Research by reducing wall reactions (Eisele and Tanner., 1993), by reducing the background signal (Tanner and Eisele., 1995), and by developing a better calibration system (Tanner et al., 1997). Mauldin et al. (1998) modified the CIMS for measurement at an aircraft platform during the First Aerosol Characterization Experiment (ACE1), and Edwards et al. (2003) further upgraded the calibration system. Based on the design of Tanner et al. (1997), another two CIMS instruments were developed at the Meteorological Observatory Hohenpeissenberg, Germany, by Berresheim et al. (2000) and at the National University of Ireland Galway by Berresheim et al. (2013). Kukui et al. (2008) developed a new version of the CIMS instrument at the Centre National de la Recherche Scientifique (CNRS), France, which allowed for OH measurements in a moderately polluted atmosphere.

Despite the previous development and application of CIMS for OH measurements, applications of this technique remain challenging, and are hindered by a lack of detailed experimental procedures to make a CIMS functional. And there have been limited deployments of CIMS for ambient OH determination compared to the LIF technique, and there has been no report of OH measurements by the CIMS method in Asia. In the present work, we describe here a new CIMS system that has been tested and optimized at The Hong Kong Polytechnic University (PolyU). The instrument was built at THS, Inc (Atlanta, Georgia) with the same design as the CIMS from the group of Eisele and Tanner. The measurement principles, configurations of the CIMS instrument, and a calibration unit are described in detail. Different scavenger gases, ion sources, and primary ions detection was compared. In addition, the sensitivity and noise of the CIMS instrument to OH radicals were tested by optimizing the flow rates and voltages. Accordingly, their optimal settings were derived. Finally, the initial measurement of ambient OH measurement was presented. The results presented in this work provide detailed technical information for other researchers who wish to apply the CIMS to ambient OH measurement. To our knowledge, this instrument is the first OH measuring CIMS in Asia.

2. Measurement principles

The measurement of hydroxyl radical (OH) in this study was made with a chemical ionization mass spectrometry (CIMS) technique, which has been described previously (Tanner et al., 1997; Sjostedt et al., 2007). Briefly, the ambient OH is converted to H_2SO_4 by adding SO_2 into the sample air flow, which initiates the following reaction sequence in the presence of oxygen and water vapor:

$$OH + SO_2 + M \rightarrow HSO_3 + M \qquad (R1)$$

$$HSO_3 + O_2 \rightarrow SO_3 + HO_2 \quad \text{(R2)}$$

$$SO_3 + 2H_2O \rightarrow H_2SO_4 + H_2O \quad \text{(R3)}$$

To mitigate interference by ambient H_2SO_4, a scavenger gas is periodically added into the sample air flow to remove OH radicals. Then, H_2SO_4 produced from the reaction of OH and SO_2 can be obtained:

$$[H_2SO_4]_{OH} = [H_2SO_4]_{TS} - [H_2SO_4]_{BS} \quad \text{(E1)}$$

$[H_2SO_4]_{TS}$ and $[H_2SO_4]_{BS}$ are H_2SO_4 concentrations with and without adding scavenger gas in the front injector, respectively. (See Section 3.1.1 for details)

Apart from the interference from the pre-existing H_2SO_4, the reactions of NO with ambient or Rection 2 produced peroxy radicals (HO_2+RO_2) can produce OH in the sample flow (Sjostedt et al., 2007):

$$RO_2 + NO + O_2 \rightarrow R'CHO + HO_2 + NO_2 \quad \text{(R4)}$$

$$HO_2 + NO \rightarrow OH + NO_2 \quad \text{(R5)}$$

To reduce the positive bias from Reaction 5, another scavenger gas is added into the sample flow after SO_2 to scavenge recycled OH radicals.

The H_2SO_4 is then converted into HSO_4^- by chemical ionization in reaction with the NO_3^- primary reactant ions:

$$H_2SO_4 + NO_3^- \cdot (HNO_3)_m \cdot (H_2O)_n \rightarrow HSO_4^- \cdot (HNO_3)_m(H_2O)_n + HNO_3 \quad \text{(R6)}$$

$NO_3^- \cdot (HNO_3)_m \cdot (H_2O)_n$ are cluster ions with m and n mostly of 0-2 and 0-3 (Berresheim et al., 2000). These cluster ions are generated by the reaction of HNO_3 vapor with electrons (Fehsenfeld et al., 1975):

$$HNO_3 + e^- \rightarrow NO_2^- + OH \quad \text{(R7)}$$

$$HNO_3 + NO_2^- \rightarrow NO_3^- + HONO \quad \text{(R8)}$$

$$NO_3^- + (HNO_3)_m + (H_2O)_n + M \rightarrow NO_3^- \cdot (HNO_3)_m \cdot (H_2O)_n + M \quad \text{(R9)}$$

Where e^- is emitted from an ion source. The OH radical (artificial OH) formed from primary ion creation (Reaction 7) is not desirable and regards as noise signal, see details in Section

5.4.3. The ion clusters are subsequently dissociated by the collisional dissociation chamber (CDC):

$$NO_3^- \cdot (HNO_3)_m \cdot (H_2O)_n + M \rightarrow NO_3^- + (HNO_3)_m + (H_2O)_n + M \quad (R10)$$

$$HSO_4^- \cdot (HNO_3)_m \cdot (H_2O)_n + M \rightarrow HSO_4^- + (HNO_3)_m + (H_2O)_n + M \quad (R11)$$

The OH is finally detected by a mass spectrometer system as HSO_4^- at 97 m/z.

3. CIMS system

Figure 1 shows the schematic of our CIMS system, which including a sample inlet system and a mass spectrometer system. The sample inlet system has two regions: chemical conversion region and chemical ionization region. The chemical conversion region is where H_2SO_4 formed by the conversion reaction of OH and SO_2. Then the H_2SO_4 converted in to HSO_4^- ion cluster in chemical ionization region. The mass spectrometer system consists of three parts including a collisional dissociation chamber (CDC) for ion cluster dissociation, an ion guide chamber (IGC) to refocused the ions, and an ion detection chamber (IDC).

3.1. Sample inlet

As shown in Figure 1, during OH measurements, air sample at ambient temperature and pressure is first drawn into a 5 cm diameter, 32 cm long stainless-steel tube. A turbulence-reducing scoop is attached in the front of the tube. The flow velocity at center of the tube is 5 m/s, which is measured manually using a pitot. The central part of the air is then drawn through a 1.6 cm diameter stainless steel inlet into the chemical conversion region with the flow rate being determined by a mass flow controller (MKS, MFC company). The excess flow in the tube is vented back into the atmosphere via the inlet blower.

3.1.1 Chemical conversion region

The chemical conversion region in Figure 1 is equipped with two pairs of stainless steel needle injectors that are placed in opposite positions. The first (front injectors) pair is installed at a 69 mm distance from the stainless sample inlet. The distances between the first (front) and second (rear) pairs are 25.8 mm. To measure OH radicals, SO_2 is continuously added into the sample flow at the front injectors to convert OH into H_2SO_4 (Reactions 1-3). The purity of SO_2 is 0.9 vol.%.

As discussed above, to eliminate the ambient H_2SO_4 interference, another flow is added through a zero-dead space four-way electrically operated valve, which is automatically

switched the injection positions of scavenger gas and pure N_2 every 3 minutes (see the pulsed flow in Figure 1). When the scavenger gas is added through the front injectors to the sample flow, N_2 is switched through the rear injectors. The CIMS is then running in background mode. Under this condition, atmospheric OH simultaneously reacts with SO_2 and the scavenger gas, with the reaction of OH with scavenger gas being much faster than SO_2. This configuration produces background signal (BS) from the interferences of atmospheric H_2SO_4 and the ion source, with negligible contribution from atmospheric OH. When the scavenger gas and N_2 are switched into the sample flow through the rear and front injectors, respectively, CIMS is running in the signal mode. Atmospheric OH is all converted by SO_2 and the total signal (TS) is produced. In addition, another flow of scavenger gas is added continuously into the sample flow through the rear injectors to scavenge OH radicals generated from Reaction 5. The OH concentration is obtained from the ratio of the difference between the total signal and the background signal to the primary ion (NO_3^-) signal. (Tanner and Eisele, 1995):

$$[\mathrm{OH}] = \frac{1}{C} \times \frac{\{\mathrm{HSO_4^-}\}_{\mathrm{TS}} - \{\mathrm{HSO_4^-}\}_{\mathrm{BS}}}{\{\mathrm{NO_3^-}\}} \quad \text{(E2)}$$

Where the square brackets and text braces denote concentrations and signal counts, respectively. C is the calibration factor. As discussed in Berresheim et al. (2000), the absolute concentration of the H_2SO_4 and reagent ion (NO_3^-) is not required as the OH concentration is determined based on their relative signal strength and the calibration factor.

3.1.2 Chemical ionization region

The sample flow through the chemical conversion region is then drawn into the chemical ionization region and mixed with the sheath gas (Figure 1). The sheath flow is continuously drawn into the same region through an annular space between 3.5 cm o.d. and 1.2 cm o.d. stainless steel tubes by a diaphragm pump (KNF-813). These tubes are concentric with the downstream end of the chemical conversion region. The sheath gas is produced by a zero-air generator (Thermo Electron Corporation, Model 111) attached with active charcoal and silica gel to remove trace gases such as SO_2 and NO_x. Before entering the ionization region, HNO_3 vapor and the scavenger gas are added continuously to the sheath gas. The HNO_3 vapor is obtained by N_2 carrier gas passing through the headspace of a reservoir of concentrated liquid HNO_3. When HNO_3 doped sheath gas passes through the ion source (Figure 1), $\mathrm{NO_3^-} \cdot (\mathrm{HNO_3})_\mathrm{m} \cdot (\mathrm{H_2O})_\mathrm{n}$ reactant ions are produced by the reaction of HNO_3 and electrons (Reactions 7-9). Additionally, the N_2 carried HNO_3 is also added through the rear injector to

maintain the ion cluster distribution and further improve the stability of the reagent ion signal (Sjostedt et al., 2007).

The $NO_3^- \cdot (HNO_3)_m \cdot (H_2O)_n$ reactant ions then react with H_2SO_4 molecules from the sample air to form $HSO_4^- \cdot (HNO_3)_m(H_2O)_n$ cluster ions in the chemical ionization region according to Reaction 6. Voltages are applied to the sample and sheath flow tubes to produce an electrical field to force the reactant ions to the center of the chemical ionization region and enhance the interaction of reactant ions with H_2SO_4. The optimization of voltages for better sensitivity is shown in Section 5.4.2.3.

The total flow (Figure 1) is then exhausted at the end of the chemical ionization region through diaphragm pumps (Thomas, SK-668) and controlled by an MFC. To prevent the HNO_3 vapor from corroding the pump and MFC and polluting the ambient air, the exhaust flow is first filtered through active charcoal cartridges and then vented back into the atmosphere at a distance of >10 m from the sampling point. A small portion of the total flow is drawn into the mass spectrometer system through a 101.6 um diameter pinhole. A small counterflow of N_2 buffer gas is added on the atmospheric pressure side of the pinhole (Figure 1) to prevent unwanted clusters and molecules from entering the pinhole (Berresheim et al., 2000). Voltages are added at the positions of N_2 buffer and pinhole to force the ions into the mass spectrometer system.

3.2. Mass spectrometer system

The mass spectrometer system is separated into three differentially pumped chambers with two adjacent chambers being connected through a 4 mm pinhole (Figure 1). The first chamber behind the pinhole is a collisional dissociation chamber (CDC). The pressure of the CDC is typically maintained at around 0.5 hPa through a drag pump (Adixen, MDP 5011) and a scroll pump (Agilent Technologies, IPD-3). The CDC has a high ion kinetic energy (i.e. high electric field to number density ratio), and most of the entered cluster ions (e.g. $HSO_4^- \cdot (HNO_3)_m(HO_2)_n$ and $NO_3^- \cdot (HNO_3)_m \cdot (HO_2)_n$) are dissociated in the CDC through Reactions 10-11.

The second chamber is an octopole ion guide high vacuum chamber (IGC). In this chamber, the pressure is maintained at about 1.3×10^{-3} hPa through a turbo molecular pump (Agilent Technologies, TwisTorr 304 Fs) and the same scroll pump mentioned above. Here, the ions from the CDC are refocused by an octopole ion guide and transported to the third chamber.

The third chamber (IDC) contains a quadrupole mass filter and detector with attached signal amplifier electronics. The mass-selected ions of the quadrupole are amplified and detected by a channeltron ion multiplier, and then counted based on standard techniques (Sjostedt et al., 2007). This chamber maintains a pressure of about 2.6×10^{-5} hPa through another turbo molecular pump and the same scroll pump.

4. Calibration

4.1 Calibration principle

The calibration of the CIMS (Figure 2a) is achieved by controlled concentrations of OH radicals, which is produced through photolysis of water vapor by 184.9 nm light (Tanner and Eisele, 1995):

$$H_2O + h\nu\ (184.9\ \text{nm}) \rightarrow OH + H \qquad \text{(R12)}$$

$$H + O_2 + M \rightarrow HO_2 + M \qquad \text{(R13)}$$

The calibration factor C is then determined based on the produced OH concentrations and detected signals of HSO_4^- and NO_3^- according to E2.

4.2 Calibration unit

Figure 2 shows the main components of the calibration unit. The unit is consisted by a cuboid stainless steel tube, a hygrometer and an optical element. The length of the cuboid stainless steel tube is 52 cm with 1.6 cm side length. The high-precision capacitance humidity measurement hygrometer (Vaisala, HMP100) is connected at the front of the tube to measure the temperature T and dew point temperature T_d of the mixed air. The optical elements are mounted at the end of the tubes (air outlet side) to minimize the wall loss during calibration. This element consists of a Pen Ray mercury lamp (Analytik Jena, UVP Pen Ray) and a bandpass filter. The bandpass filter blocks most of the emitted photons except those at 184.9 nm. Finally, the transmitted light enters the tube and photolyzes water vapor to produce OH radicals according to Reaction 12. The mixing ratio of water vapor in the air flow is controlled through the mix of the dry synthetic air and humidity air from a water bubbler.

4.3 Calibration quantification

4.3.1 OH quantification

The concentrations of OH radicals produced from the water vapor photolysis reaction can be described as follow:

$$[\mathrm{OH}] = I \times t \times \sigma_{\mathrm{H_2O}} \times \phi_{\mathrm{H_2O}} \times [\mathrm{H_2O}] \quad \text{(E3)}$$

Where I and t are the photon intensity (unit: photons s^{-1} cm^{-2}) and the reaction time of H_2O photolysis, respectively. The determination of *It* is described in Section 4.3.2. [OH] and [H_2O] are the concentrations of OH radicals and water vapor, respectively, $\sigma_{\mathrm{H_2O}}$ is the photolysis cross-section of water vapor at 184.9 nm (7.22×10^{-20} cm^2, Cantrell et al., 1997) and $\phi_{\mathrm{H_2O}}$ represents the photolysis quantum yield, which is assumed to be 1.0 at 184.9 nm. [H_2O] is calculated according to the temperature (T), saturated water vapor pressure ($P^{\circ}_{H_2O}$) and relative humidity (RH) of the mixed air flow (Kurten et al., 2012).

4.3.2 *It* quantification

The product *It* is determined based on the chemical actinometry method (Figure 2b). This method measures NO_x generated from N_2O photolysis with the same calibration unit under the same condition as that for the CIMS calibration. Since N_2O photolysis and H_2O photolysis require the same photon intensity (184.9 nm), product *It* of H_2O photolysis can be determined by measured NO_x and N_2O mixing ratios produced by N_2O photolysis (Edwards et al., 2003).

Briefly, high purity N_2O (99.9%) mixed with dry synthetic gas flows into the calibration unit. The photolysis of N_2O generates NO_x through the following reactions (Edwards et al., 2003):

$$\mathrm{N_2O} + h\nu\ (184.9\ \mathrm{nm}) \rightarrow \mathrm{N_2} + \mathrm{O}(^1\mathrm{D}) \quad \text{(R14)}$$

$$\mathrm{O}(^1\mathrm{D}) + \mathrm{O_2} \rightarrow \mathrm{O}(^3\mathrm{P}) + \mathrm{O_2} \quad \text{(R15)}$$

$$\mathrm{O}(^1\mathrm{D}) + \mathrm{N_2} \rightarrow \mathrm{O}(^3\mathrm{P}) + \mathrm{N_2} \quad \text{(R16)}$$

$$\mathrm{O}(^3\mathrm{P}) + \mathrm{O_2} + \mathrm{M} \rightarrow \mathrm{O_3} + \mathrm{M} \quad \text{(R17)}$$

$$\mathrm{O}(^1\mathrm{D}) + \mathrm{N_2O} \rightarrow 2\mathrm{NO} \quad \text{(R18)}$$

$$\mathrm{O}(^1\mathrm{D}) + \mathrm{N_2O} \rightarrow \mathrm{N_2} + \mathrm{O_2} \quad \text{(R19)}$$

The O_3 produced from Reaction 17 could oxidize NO to NO_2. Therefore, the photolysis of N_2O eventually converts it to NO_x which is concurrently measured by a commercial NO_x detector

(Thermo, Model 42i-TL) The combined product *It* is a function of the mixing ratios of N_2O, N_2, O_2, and produced NO_x:

$$It = \frac{(K_{15} \times [O_2] + K_{16} \times [N_2] + (K_{18} + K_{19}) \times [N_2O]) \times [NO_X]}{2 \times K_{18} \times \sigma_{N_2O} \times \phi_{N_2O} \times [N_2O]^2} \quad \text{(E4)}$$

Where K_{15}, K_{16}, K_{18}, K_{19} are the rate constants of Reaction 15, 16, 18 and 19, respectively. σ_{N_2O} is the absorption cross-section of N_2O and ϕ_{N_2O} is the photolysis quantum yield. The values for them can be found in previous study (Kurten et al., 2012).

Ideally, the N_2O actinometry experiment should be conducted with the same flow rate as in the H_2O photolysis experiment such that the reaction time can be the same. However, at the flow rate suitable for CIMS calibration (10 slpm), the concentration of NO_x produced from N_2O photolysis is near the detection limit of the NO_x detector. Hence, the N_2O actinometry experiment was carried out at a lower flow rate (3 and 6 slpm) to increase the reaction time for photolysis and then the NO_x production. The *It* values for lower flow rate (It_{HLOW}) and higher flow rate (It_{HIGH}) have the following relationship:

$$It_{HIGH} = \frac{FR_{LOW} \times It_{LOW}}{FR_{HIGH}} \quad \text{(E5)}$$

where FR_{LOW} and FR_{HIGH} represent different flow rate. Based on this equation, It_{HIHG} can be obtained by scaling It_{LOW} with the ratio of FR_{LOW} and FR_{HIGH}. The E5 is validated in the next section.

4.3.2 *It* determination

Figure 3 shows the results of N_2O actinometry experiment. Figure 3a shows the NO_x produced as the function of N_2O mixing ratios from 10% to 15% at different flow rates (FR_{N_2O} = 3, 6, and 10 slpm). Generally, an increase in the N_2O mixing ratio or a decrease in reaction time (lower flow rate) led to more production of NO_x. In figure 3b, the product *It* corresponding to different flow rate was calculated according to E4 based on the result in Figure 3a. The product *It* linearly increased with the inverse of the flow rate, which validates the linear dependency between product *It* and inverse of the flow rate shown by E5. This linear dependency is consistent with the result in Kurten et al. (2012). In addition, the product *It* was independent of the N_2O mixing ratios in range of 10% to 15% (Figure 3c). Based on the E5, the flow rate scaled *It* (It_{HIGH}) is calculated from It_{LOW} in Figure 3b multiplying the ratio of FR_{LOW} (3, 6, and 10 slpm, respectively) to FR_{HIGH} (10 slpm). The *It* varied from 1.37 to 1.53 x 10^{11} at

different flow rates and N_2O mixing ratios. The mean value of 1.46 x 10^{11} photon cm^{-1} was adopted for It_{HIGH}.

4.3.3 Calibration result

Figure 4 shows an example of a typical procedure for determining the calibration factor. The instrument signals were continuously measured by adjusting H_2O concentrations without changing other parameters. The different OH concentrations were calculated according to E3. For each step, the signal intensities (in Hz) of HSO_4^- and NO_3^- were collected for 6 minutes with 3 minutes each for background mode and signal mode. The calibration factors were determined from the calculated OH concentrations and signal intensities based on E2. The red dots in Figure 4 represent the average calibration factors for every 6 minutes. The result shows that the calibration factors different steps were very close, ranging from 1.60 to 1.69x10^{-10}, and were independent of water vapor concentrations. The averaged calibration factor for our CIMS is 1.64x10^{-10} molecule/cm^{-3}.

5. CIMS optimizations

As shown in Figure 1, the CIMS system is complicated, and its performance is affected by different parameters and components. In this section, we present the results of tests for different types of ion sources and scavenger gases (propane and C_3F_6), comparison of primary ions detection, and optimization of the instrument sensitivity and noise.

5.1. Ion source

Radioactive ion source (^{210}Po or ^{241}Am) and corona discharge source (corona ionizer) have been used as the ion source in previous studies (Berresheim et al., 2000; Sjostedt et al., 2007; Kukui et al., 2008). In this study, ^{210}Po and corona sources were compared.

^{210}Po emitted alpha particles that interact with the carrier gas to quickly form thermalized electrons and positive ions (Fehsenfeld et al., 1975). The formed electrons react with O_2 and then HNO_3 to produce $NO_3^- \cdot (HNO_3)_m \cdot (H_2O)_n$ reactant ions. ^{210}Po was used due to its low OH interference and ease of installation. Corona ionizer generates NO_3^- by discharge formed between a tungsten needle and a 1 mm diameter plate 3 mm from the needle tip (Kukui et al., 2008). The corona source has the advantage of producing much higher concentrations of $NO_3^- \cdot (HNO_3)_m \cdot (H_2O)_n$ primary ions compared with radioactive ^{210}Po or ^{241}Am foils, which leads to higher concentrations of HSO_4^- and higher signal intensities (and higher sensitivities). However, the corona discharge source is known to produce a significant amount of neutral

species including OH radicals (artificial OH), which means the noise is relatively high (Kukui et al., 2008). We compared a ^{210}Po ions source and a corona source (Figure S1). The result showed that the detection limit of the CIMS with the ^{210}Po ion source was lower than that with the corona source due to larger noise in the corona source. We previously applied the corona source in the same CIMS to measure peroxy radicals (RO_2 and HO_2), and the noise level was acceptable compared to the ambient concentration of peroxy radicals. For OH measurement, although a scavenger gas was added in the sheath flow to remove most artificial OH radicals, the remaining interferences were still high compared to ambient OH concentrations.

In this study, ^{210}Po foils were chosen as the ion source in our CIMS system. It should be noted, however, that a radioactive source like ^{210}Po often subjects to strict health safety regulations, and the users need apply a permit to use and transfer the radioactive source. In addition, ^{210}Po undergoes alpha decay to stable ^{206}Pb with a half-life of about 140 days. Therefore, in order to keep stable signal intensities for primary ions, the ^{210}Po foils need to be replaced regularly.

5.2 Scavenger gases

As discussed in Section 3, scavenger gas is very important for OH measurement by CIMS. Propane, C_3F_6, and NO2 have been used by different groups (Berresheim et al., 2000; Sjostedt et al., 2007; Kukui et al., 2008). However, there have been no reports on comparisons of these three scavenger gases. In this study, The first two were compared. (We could not purchase high purity NO_2 due to health safety restriction in Hong Kong). The scavenger gas was added in two positions for different purposes. In the sheath flow, the scavenger gas reduced the interference of artificial OH from the ion source; in the sample flow, it terminated the OH conversion (in the rear injector) and eliminated the ambient OH to determine background (in the front injector).

Figure 6 shows that 99.95 vol.% pure propane (Harvest Wise Gases (H.K.) Limited) added in sheath flow could effectively (~80%) remove artificial OH radicals from the ion source with the remaining contributing a low and stable signal at 97 m/z. For the OH removal efficiency of in the sample air, propane could remove OH at 97.7% of OH even at the concentrations of two orders of magnitude higher than ambient OH level (for more details, see Section 5.4.3). The signal intensity of the primary ions was not affected by the added propane and kept stable (Figure S2).

For C_3F_6, although its OH removal efficiency was also high, it suppressed the signal intensities detected by the mass detector. This suppression recovered after time when the detector was new (figure not shown). However, when the detector was aged, such suppression triggered a

continuous decrease of the reagent signal as shown in Figure S2a. In this case, the change of reagent ions detection signal can avoid such decrease (Figure S2b).

Based on the above test results and considering that propane is inexpensive and easy to purchase, propane was selected as the scavenger gas for our CIMS.

5.3 Primary ions detection

Determination of the OH concentrations needs to use the signal intensities of NO_3^- ions according to E2. Some previous researchers traced the NO_3^- ions on the signal intensities at 62 m/z (Kukui et al., 2012; Sjostedt et al., 2007; Tanner et al., 1997). We found that the concentrations of NO_3^- in the inlet system were extremely high. Even though a small portion of the NO_3^- ions were finally detected by the mass detector, the signals were still very strong. After operating the CIMS with detecting the signal of NO_3^- ions at 62 m/z about half a year, all signals from the channeltron detector dropped significantly which may be due to the accelerated aging of the detector by the high concentrations of NO_3^- ions. Therefore, the isotopic signal ($N^{18}O_3^-$) at 64 m/z was chosen to detect NO_3^- primary ions for extended operation. The signal intensity at 64 m/z is lower than at 62 m/z by about a factor of 167.

5.4 Instrument sensitivity and noise

5.4.1 Sensitivity optimization

The sensitivity (S) of the CIMS instrument to the OH radicals depends on the reaction efficiency of OH and SO_2 in chemical conversion region (f(CE)), the conversion efficiency of H_2SO_4 to HSO_4^- in chemical ionization region (f(IE)), and the transmitted efficiency of HSO_4^- from sample inlet to mass spectrometer system (f(TE)):

$$S \sim f(CE) \cdot f(IE) \cdot f(TE)$$

f(CE) is dependent on the reaction time and the SO_2 concentration of the conversion reactions (R1-3). f(IE) is affected by the flow dynamics, which determines the mixing of flows, and the electric field inside the ionization region, which forces the $NO_3^- \cdot (HNO_3)_m \cdot (HO_2)_n$ primary ions to the center of the region for H_2SO_4 ionization. The f(CE) is related to the N_2 buffer and the induces electric field in the pinhole area. In this work, the f(CE) is first optimized for the maximum conversion of the ambient OH to H_2SO_4 by adjusting the SO_2 flow and the sample flow rate. Then, to achieve best f(IE) for H_2SO_4 ionization, the flow dynamic and electric field

are optimized by adjusting the sample/sheath flow ratio and the voltages applied to sample and sheath flow. Finally, the N_2 buffer flow rate and the voltages of the pinhole are adjusted to control the f(TE) to determine the amounts of ions entering the detector. During the optimization, the calibration tube is applied to produce OH radical and control its concentration.

5.4.2 Conversion efficiency

Figure 5a shows the normalized signal intensity (NSI) at 97 m/z for HSO_4^- as a function of the flow rate of SO_2 (0.9 vol.%). The NSI first increased with increased SO_2, and reached a stable level at a flow rate > ~2.5 sccm, which did not vary with the relative humidity. This result indicates that the SO_2 concentration at the flow rate of 2.5 sccm was adequate to convert sampled OH to H_2SO_4. Since the concentration of OH radical produced by the calibration unit during optimization was 1 to 2 magnitude higher than in that in ambient condition, the 2.5 sccm flow of SO_2 is adequate for ambient measurement. We set the SO_2 flow rate at 5 sccm with a factor of 2 margin, following the previous study (Sjostedt et al., 2007). With this flow rate, the concentration of SO_2 in sample flow is 12 ppm.

The effects of the sample flow rate on NSI are shown in Figure 5b. During adjusting the sample flow rate, if the sheath flow rate remains the same, the conversion time and the flow dynamics will be affected. Thus, in order to show the effect of conversion time to NSI only, the sheath flow was adjusted along with the sample flow to maintain the sample/sheath flow ratios and control the f(IE) in Figure 5b. Briefly, the NSI increased with the decrease of sample flow rate, which can be explained by a longer OH conversion time (R1-3) and a higher f(CE) at a lower flow rate. However, the increased reaction time will also increase the OH interference produced from HO_2 recycling in the presence of NO in sample air. Previous studies usually kept the reaction time less than 60 ms to mitigate such interference (e.g. Tanner et al., 1997). After considering the reaction time and interference, the sample flow rate was set at 3.7 slpm, which gives a reaction time of ~47 ms. After the above selection of the SO_2 concentration and sample flow rate, the optimal f(CE) is determined.

5.4.3 Ionization efficiency

Figure 5c shows the NSI as a function of the ratio of sample flow to sheath flow in the ionization region. The NSI firstly increased and then decreased with the increased ratio, with a peak value at a sample/sheath flow ratio of 0.3. This optimized ratio was independent of the total flow rates from 12 to 21 slpm. This ratio produced a turbulent flow in the chemical

ionization region. Such flow dynamics facilitates a fast mixing of the reactants, and enhances the f(IE) of H_2SO_4 as well as the NSI at 97 m/z (Tanner and Eisele, 1995; Tanner et al., 1997).

Figure 5d-e shows the effects of voltages applied to the sample and sheath flow on NSI. The NSI first increased and then decreased as the increase of difference in voltage between the sample and sheath flow (figure 5d). At the voltage difference of 48 V, the peak NSI was achieved, and this voltage difference is selected. Figure 5e shows the NSI increased with the negative sheath voltage and then kept stable with sheath voltage < -70V. This shows that when it is negative charged, it is the voltage difference but not the exact voltage that affects the NSI. In our studies, we set the inlet and sheath voltages at -32 and -80 V, respectively. The cross interactions of sample/sheath flow and voltages on NSI were also evaluated (see Figure S3). The result shows that the highest NSI was achieved when the sample/sheath flow ratio was close to 0.3, independent of the voltages. The optimized f(IE) of the CIMS is achieved by the above selections of the flow ratio and electric field.

5.4.4 Transmission efficiency

The N_2 buffer flow rate controls the proportion of sample air in dry N_2 (refer to figure 1), thereby affecting amount of ion clusters in the sample air entering the mass detector. Figure 5f shows that the NSI increased with the decreased the buffer flow rate, as expected. However, a lower flow rate of N_2 buffer gas also allows more undesired neutral molecules and particles in sample air to enter the mass spectrometer (Berresheim et al., 2000). With these considerations, the flow rate of N_2 buffer gas was set as 440 sccm. To force the ions to the center of the pinhole, the voltage applied to before and on the pinhole was set at -70V and -40V, respectively.

5.4.5 Noise minimization

After optimization of CIMS's sensitivity, noise minimization is needed to reduce the signal that is not related to the ambient OH concentration. As discussed above, the noises for OH measurements include H_2SO_4 in ambient air and artificial OH produced by the ion source. These noises can be mitigated by adding a scavenger gas in the sheath flow to eliminate artificial OH and in sample flow to quantify ambient H_2SO_4 (Figure 1). Below we determine the optimal flow rates for the scavenge gas.

Figure 6 shows the HSO4- signal intensity as a function of propane flow rates in sheath flow, with N_2 gas as the sample air. When propane was not added, the artificial OH concentration from the ^{210}Po ion source was ~3.5×10^6 molecules cm^{-3}, which is comparable to the typical OH

concentrations in ambient environments. When propane was added into the sheath gas, the artificial signals were reduced with the increasing propane flow and kept stable at ~1×10^6 molecules cm^{-3} when the flow rate was higher than 1 sccm. We thus set a flow rate of 2 sccm for propane in the sheath flow.

Figure 7 shows the removal efficiency (RE) of OH by propane added in the sample flow as a function of the propane flow rates. The OH radicals were produced by the calibration unit described in Section 4.2. The RE increased with the increased propane flow rate initially and levelled off at the flow rate > 1 sccm. We adopt the flow rate of propane of 2 sccm (~535 ppm), which led to ~98% removal efficiency for OH. As OH concentrations in this test are much higher than those in typical ambient air, the RE of the propane for ambient OH should be even large at the selected flow rate.

6. Detection limit and uncertainty

The detection limit can be calculated as follows,

$$DL = \frac{1}{C} \times \frac{n * \sigma}{\{NO_3^-\}} \quad \text{(E6)}$$

Where DL is the detection limit in 10^6 molecule/cm^3, C is the calibration factor, and *n* is the ratio of signal to noise S/N. σ represents the standard deviation of the signal intensity of HSO_4^- at 97 m/z, and $\{NO_3^-\}$ represents the signal intensity of NO_3^- at 64 m/z at the integration time t.

Figure 8 shows the concentrations of OH radicals and the corresponding detection limit (S/N=2, average time=6 minutes) in the laboratory. The detection limit was quite stable over the whole day and ranged from 0.08 to 0.20*10^6 molecule cm^{-3}, with an average value of approximately 0.15 *10^6 molecule cm^{-3}.

The uncertainty for the calibration factor (C) of OH measurements is dependent on the uncertainties of all the parameters involved in the calculation of the concentrations of OH radicals and the precision of the measurements of signal at 64 m/z and 97 m/z. The uncertainty was ~36% for *It* (see Figure 3), σ_{H_2O}~5% for σ_{H_2O}, <1% for ϕ_{H_2O} (Cantrell et al. 1997), and ~10% for the water concentration (Kukui et al., 2008). The precision of the measurements signal at 64 m/z and 97 m/z of the CIMS instrument (2σ) was 11% (for 6 min integration time). The overall uncertainty for the calibration factor was about 38%.

7. Field deployment of CIMS

In order to examine the performance of our CIMS in the ambient environment, we deployed the optimized instrument to an urban site of Hong Kong in April 2019 (Figure S4). The site was located on the 11th floor of a teaching building on the campus of The Hong Kong Polytechnic University (PolyU) and was surrounded by several busy roads. The sample inlet was positioned horizontally facing the south. Measurements were made with a time resolution of 10 seconds. A typical measurement sequence consisted of 3 minutes in the background mode and 3 minutes in the signal mode. Figure 9a shows the diurnal profile of OH concentrations (3-minute average) observed on April 25, 2019, and the solar radiation measured using UTA-LI200 at a time resolution of 1 minute. Figure 9b shows the measured signal intensities at 97 m/z at the signal mode and the background mode. The OH concentrations exhibited a clear diurnal profile with the highest value of ~6×10^6 molecules cm^{-3} at midday and the lowest level of ~0.25×10^6 molecules cm^{-3} at night. The OH concentrations were highly correlated to solar radiation, which was similar to previous studies (e.g. Rohrer and Berresheim, 2006; Tan et al., 2017). The 3-minute average OH concentrations were above the detection limits (0.5-2×10^6 molecules cm^{-3}) most of the daytime, except during a cloudy period (08:00 to 10:00) (Figure 9a). This preliminary result demonstrated the capability of our CIMS for measuring ambient OH on a clear day in an urban environment. However, Figure 9b reveals that the contribution to instrument background from ambient H_2SO_4 was significant at the site, which raised the detection limit and measurement uncertainty (to 51%). The ambient H_2SO_4 concentration (10 sec average), which was estimated by the normalized background signal divided by the OH calibration factor, varied from 2.6 x 10^5 in before sunrise to 8 x 10^6 molecule/cm^3 in mid-day (figure not shown). Future work will make use of isotopically labelled $^{34}SO_2$ to eliminate H_2SO_4 interference (Eisele and Tanner, 1991).

8. Summary and conclusions

To measure the atmospheric OH radicals, we have developed the first chemical ionization mass spectrometry (CIMS) system in Asia. It is an indirect measurement technique that converts OH radicals to HSO_4^- which is detected by the ion-assisted mass spectrometry method. In addition, the calibration system has been developed. A series of comparisons of different ion sources, scavenger gases, and primary ions detection have been conducted to optimize the performance of the CIMS for OH measurement. The sensitivity is dependent on the efficiencies of conversion reaction, ion conversion, and ion transmission which have been improved by optimizing the flow rates of a myriad of gases and voltages in various components. An initial

field test has demonstrated the capacity of this instrument in measuring ambient OH in an urban site on clear days. The main findings on the key parameters are summarized below.

(1) ^{210}Po has lower artificial OH interference compared to a corona ionizer, and it is adopted as the ion source.

(2) C_3H_8 is a better OH scavenger than C_3F_6 because of the high elimination efficiency and signal stability of C_3H_8.

(3) A set of procedures has been developed to optimize the flow rates of sample gas, sheath gas, and N_2 buffer gas, voltages on the sample inlet system and the concentration of SO_2 conversion gas with the aim to increase instrument's sensitivity and reduce noise.

(4) The CIMS instrument achieved a detection limit of 0.15×10^6 molecules cm^{-3} and uncertainty of 38% (S/N=2) under laboratory conditions. In the field, the detection limit increased to about 0.15×10^6 molecules cm^{-3} on clear days, with the overall accuracy of about 51%.

(5) Future work includes more field experiments in various environments and utilization of isotopically labelled $^{34}SO_2$ to eliminate the H_2SO_4 interference.

We note that the optimal values of instrument parameters may differ in different CIMS systems due to the different design and/or configurations, the test procedures and results from our study provide a useful reference to other researchers who wish to apply CIMS technique to measure atmospheric OH radicals.