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A hydroxyl radical detection system using gas expansion and fast gating laser-induced fluorescence techniques

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ABSTRACT

An OH radical measurement instrument based on Fluorescence Assay by Gas Expansion (FAGE) has been developed in our laboratory. Ambient air is introduced into a low-pressure fluorescence cell through a pinhole aperture and irradiated by a dye laser at a high repetition rate of 8.5 kHz. The OH radical is both excited and detected at 308 nm using A-X(0,0) band. To satisfy the high efficiency needs of fluorescence collection and detection, a 4-lens optical system and a self-designed gated photomultiplier (PMT) is used, and gating is actualized by switching the voltage applied on the PMT dynodes. A micro channel photomultiplier (MCP) is also prepared for fluorescence detection and can interchange with the gated PMT. Then the weak signal is accumulated by a photon counter in a specific timing. The OH radical excitation spectrum range in the wavelength of 307.82–308.2 nm is detected and the excited line for OH detection is determined to be $Q_1(2)$ line. The calibration of the FAGE system is researched by using simultaneous photolysis of H_2O and O_2. The minimum detection limit of the instrument using gated PMT is determined to be 9.4×10^5 molecules/cm^3, and the sensitivity is 9.5×10^{-7} cps/(OH·cm^{-3}), with a signal-to-noise ratio of 2 and an integration time of 60 sec, while OH detection limit and the detection sensitivity using MCP is calculated to be 1.6×10^5 molecules/cm^3 and 2.3×10^{-6} cps/(OH·cm^{-3}). The laboratory OH radical measurement is carried out and results show that the proposed system can be used for atmospheric OH radical measurement.

Introduction

The hydroxyl (OH) radical is known as the most potential oxidizing agent for many chemical species in the lower atmosphere. Its concentration has been estimated to be approximately in the 1×10^6 molecules/cm^3 range (Heard and Pilling, 2003; Stone et al., 2012; Amedro et al., 2012). The OH radical is involved in many atmospheric chemistry progresses through reactions with O_3, CO, CH_4, NO_2, and numerous non-methane hydrocarbons (Hofzumahaus et al.,

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2009; Whalley et al., 2010; Khan et al., 2011; Lu et al., 2013). The chemical mechanisms for the formation and consumption of OH are very complex, and understanding the various pathways involved is important to accurately model atmospheric chemistry and predict atmosphere evolution. Measuring OH radical has proven to be challenging in atmospheric chemistry because of the high reactivity, short lifetime, and extremely low concentration of this radical.

Numerous research groups have developed systems for measuring tropospheric OH radicals, resulting in the fabrication of several reliable instruments. These techniques mainly include laser-induced fluorescence (LIF) [in particular, fluorescence assay by gas expansion (FAGE)] (Kanaya et al., 2001; Novelli et al., 2014; Fuchs et al., 2016), differential optical absorption spectroscopy (DOAS) (Dorn et al., 1996; Fuchs et al., 2012), chemical ionization mass spectrometry (CIMS) (Mauldin et al., 2003), ^{14}CO oxidation (Campbell et al., 1995) and salicylic acid scrubbing (Liu and Wang, 2008). Among these methods, FAGE has been demonstrated as an effective tool in the detection of atmospheric OH radical because of its high sensitivity, good selectivity, and low detection limit. Compared to other techniques, FAGE can also measure the concentration of a series of radical like OH, HO_2, and RO_2, which is important means to research the radical reaction activity and its atmospheric chemical mechanism (Fuchs et al., 2008; Whalley et al., 2013; Weinberg et al., 2015).

FAGE technique used for OH radical measurement is first developed by Hard (Hard et al., 1984). Several groups have designed and improved their own instruments for more than 20 years, including techniques for instrument optimization (Holland et al., 1995; Kanaya et al., 2001; Dusanter et al. 2009a; Novelli et al., 2014), calibration studies (Hard et al., 2002; Dusanter et al., 2008), interference studies (Ren et al., 2004; Fuchs et al., 2011), and comparisons with other instruments (Dorn et al., 1996; Mauldin et al., 2003; Schlosser et al., 2009). FAGE instruments have been used in various field campaigns for different environments (Kanaya et al., 2007; Dusanter et al. 2009b; Vaughan et al., 2012). It has a detection limit of an order of magnitude of 10^5 molecules/cm^3 and has proved to be a reliable tool to study the tropospheric OH radical. Moreover, numerous data for atmospheric chemistry modeling or further research on the mechanism of atmospheric reactions have been accumulated. Reliable FAGE systems have been developed by several universities and institutes, but few related studies have been conducted in China, where the process of atmospheric chemistry is more complicated due to its climatic conditions and industrial development. Peking University has recently performed several OH field measurements by FAGE in Beijing District and Pearl River Delta, and researched their chemistry progress combined with the local condition (Lou et al., 2010; Lu et al., 2012, 2013).

A new OH radical instrument based on FAGE is described in this paper. Each part of the FAGE instrument is designed and established in our laboratory. The OH radical is both excited and detected at 308 nm of the A-X(0,0) band. Ambient air is sampled through a pinhole and excited fluorescence in a low-pressure cell. This instrument use a gated photomultiplier (PMT) as a detector, which is actualized by a home-made gating circuit by switching the voltage applied on the dynodes of the PMT. And a commercial micro channel photomultiplier (MCP) has also prepared for system experiment and comparison. Fluorescence signal is detected at a specific gated timing and accumulated by a photon counting card. The performance of the developed FAGE system has been detected in the laboratory and its calibration is researched. OH concentration is detected and analyzed, and the system is optimized to obtain a better sensitivity and detection limit to meet the requirement of ambient OH measurement.

1. Principle of FAGE technology

LIF is an efficient tool for detecting tropospheric OH radical. Based on the strong discrete line absorption spectrum of A-X(1,0) band at approximately 282 nm ($A^2\sum^+(v'=1)\leftarrow X^2\prod(v''=0)$) or A-X(0,0) band ($A^2\sum^+(v'=0)\leftarrow X^2\prod(v''=0)$) at approximately 308 nm, hydroxyl radicals can be selectively excited by a narrow-bandwidth laser. The amount of resonant fluorescent light subsequently emitted around 307–311 nm can be used to measure OH concentration. Most groups currently use A-X(0,0) band for excitation and detection to reduce O_3 interference.

FAGE is a pioneered improvement of the LIF technique and utilized to detect OH at low pressure. Sampling ambient air at low pressure can reduce the concentration of interference species, such as O_3 and H_2O (Stevens et al., 1994). Expanding air sample from atmospheric pressure to a few hectopascals results in an extended lifetime of OH fluorescence beyond the time region of Rayleigh, Mie, and wall scattered light. Under this condition, OH concentration is reduced to several magnitudes, and the lifetime of OH fluorescence is extended to several hundred nanoseconds (Kanaya et al., 2001; Heard, 2006). Then, the fluorescence is selectively detected by time filtering, namely a gating detector in nanosecond. Nevertheless, the main background signal is still linearly dependent on laser intensity, and the optimization is based on raising OH sensitivity while keeping the background signal as low as possible.

The major parts of this instrument include laser source combined with wavelength reference cell, fluorescence detection cell, detector, and data processing unit, which is shown in Fig. 1. The laser system is a dye laser pumped by a Nd:YVO_4 laser, which provides a 308 nm output at a high repetition rate of 8.5 kHz, and it wavelength is fixed by using a reference cell. Ambient air is introduced to the cell by a vacuum pump system, which makes the gas sampled through an inlet pinhole and expands under the nozzle, and pressure in the cell is drawn to be approximately 350 Pa. With this sampling method, this system can extend the lifetime of OH fluorescence and reduce the interference of O_3. The laser passes the cell through the laser arm, which achieves an excitation volume with the cross of the gas flow at the midpoint of the cell. Then, the fluorescence is collected by a 4-lens system and detected by a detector, while the detector is gated off when the laser pulse appears and fast turning on for fluorescence detection after laser ends. The extremely weak and short-lifetime fluorescence signal is measured by a photon counting card, with proper timing and discrimination level. Then, OH radical concentration is further processed by a computer and analyzed after calibration.

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