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Development of Fiber-Laser-Based Laser-Induced Fluorescence for Detection of SO₂

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Abstract

Gaining a quantitative understanding of many aspects of the earth's climate system requires development of new detection methods for key atmospheric species and their incorporation into chemical sensors with high sensitivity, specificity, and time response. We have initiated a research program to develop these new chemical-sensing capabilities. The species we have targetted initially are oxides of nitrogen and sulfur, specifically NO and SO₂. These molecules play a central role in the earth's climate, and anthropogenic activities (primarily fossil-fuel combustion) are the dominant source of both species. We are exploring the use of single-mode fiber lasers and amplifiers as compact, lightweight sources of tunable, narrow-bandwidth, deep-UV radiation. We have also begun spectroscopic studies to optimize UV laser-induced fluorescence for detection of SO₂ with high sensitivity and specificity.

Introduction

Current understanding of many aspects of the earth's climate system is limited by the available data: measurements of critical species and processes are required to gain a detailed and quantitative understanding of past and present climates, to assess and narrow the uncertainties in climate models, and to develop the predictive capability required to discern natural and anthropogenic influences on the future climate. Providing such measurements will require development of new diagnostic methods for key atmospheric species and their incorporation into chemical sensors with high sensitivity, specificity, and time response. We have initiated a research program to develop these new chemical-sensing capabilities.

The species we will target initially are oxides of nitrogen and sulfur, specifically NO and SO₂. These molecules play a central role in the earth's climate, and anthropogenic activities (primarily fossil-fuel combustion) are the dominant source of both species. Existing measurement methods for NO and SO₂ lack adequate sensitivity and/or time response to address many outstanding questions in studies of the earth's climate.

We are exploring the use of single-mode fiber lasers (developed for optical telecommunications) as compact, lightweight sources of tunable, narrow-bandwidth, deep-UV radiation. We have also begun spectroscopic studies to optimize laser-induced fluorescence for detection of SO₂ with high sensitivity and specificity.

The Role of NO and SO₂ in Regulating Climate

NO controls the abundance of ozone (O₃) in both the troposphere, where it catalyzes O₃ formation, and stratosphere, where it catalyzes O₃ destruction. In the upper troposphere, O₃ is an important greenhouse gas. Evidence suggests that upper tropospheric O₃ concentrations have increased by as much as a factor of two since pre-industrial times [Intergovernmental Panel on Climate Change (IPCC) 94, p. 78; IPCC 95, p. 90], with some regions of the northern hemisphere showing a 50% increase in just the past 30 years (IPCC 94, p. 98). At least some of this increase is thought to be attributable to increased emissions of NO_x (NO and NO₂), although from present measurements, "...we cannot define the importance of anthropogenic sources (transport of surface pollution out of the boundary layer, direct injection by aircraft) relative to natural sources (lightning, stratospheric input) in controlling the global NO_x distribution." (IPCC 94, p. 78). Stratospheric O₃ absorbs incoming solar UV radiation between 220 and 320 nm. The stratospheric O₃ abundance is determined by catalytic O₃ destruction cycles; the most important cycle (globally) involves reaction of O₃ and O atoms with NO_x. Depletion of stratospheric O₃ affects climate via at least two mechanisms: (i) increased flux of UV to the troposphere, which enhances production of OH, the primary atmospheric oxidant (i.e., reaction with OH removes atmospheric methane and hydrogen-containing halocarbons, which are significant greenhouse gases, as well as other reduced species); and (ii) decreased transport of O₃ into the troposphere from the stratosphere (IPCC 94, p. 81). New measurements are required to gain a detailed and quantitative understanding of the

chemistry of O_3 in both the troposphere and stratosphere, particularly of the controlling role played by oxides of nitrogen.

Sulfur compounds profoundly influence the chemistry and radiative properties of the atmosphere on local, regional, and global scales. Over half the atmospheric sulfur source is SO_2 emitted from fuel combustion and industrial activities. The fate of SO_2 once it enters the atmosphere is highly uncertain: it can be deposited on the surface (e.g., on plants or the ocean, where it affects the chemistry and biochemistry of these systems), or it can be oxidized in the air and in water droplets to sulfuric acid (H_2SO_4), the precursor to sulfate aerosols. Sulfate aerosols derived from oxidation of gas-phase sulfur compounds are estimated to constitute ~35% of the global particle mass. Tropospheric sulfate aerosols affect the earth's radiative balance by two mechanisms: (i) directly, via back-scattering of incoming solar radiation, and (ii) indirectly, via their influence on cloud formation and cloud properties. Recent research has focused on incorporation of these processes into global climate models, and radiative forcing by sulfate aerosols is a major source of uncertainty in these models. In particular, the partitioning between SO_2 deposition and oxidation to sulfate and the atmospheric and surface parameters that control the relative importance of these two processes are highly uncertain. The most direct method for measuring deposition fluxes of gases is eddy correlation, however "...a major limitation to research on surface-exchange and flux measurements is the lack of sensitive, reliable, and fast-response chemical sensors that can be used for eddy correlation flux measurements." (NSF/NASA/NOAA Global Tropospheric Chemistry Workshop). No SO_2 instrument exists with the requisite sensitivity and time response for *in situ* measurement of ambient SO_2 concentrations and fluxes throughout the atmosphere.

Experimental Results

Two types of experiments were performed:

- (1) spectroscopic studies of sulfur dioxide (SO_2), to optimize the laser-induced fluorescence (LIF) detection scheme; and
- (2) development of a compact fiber laser for generation of narrow-bandwidth, ultraviolet (UV) radiation.

The results of these studies are summarized below.

Spectroscopic Measurements

We measured absorption, fluorescence-excitation, and dispersed-fluorescence spectra of SO_2 at pressures of 7-700 Torr (the range relevant for detection throughout the atmosphere) with the bath gases N_2 and O_2 (the two most prevalent atmospheric colliders). The excitation wavelength was tuned between 210 and 220 nm, and fluorescence was detected from 210 to 400 nm.

The spectroscopic measurements were performed using a frequency-tripled dye laser (Laser Analytic Systems) pumped by an injection-seeded Nd:YAG laser (Positive Light).

The Nd:YAG laser produced pulses of ~15-ns duration at a repetition rate of 20 Hz. The dye laser (operating with DCM in methanol) produced tunable pulses at ~610-670 nm with a linewidth of ~0.05 cm⁻¹. The output of the dye laser was frequency tripled to ~215 nm using BBO crystals (Inrad Autotracker II). The intensity and polarization of the UV beam were controlled using a half-wave plate and a polarizer; the pulse energy was attenuated to avoid saturation of the transitions.

The UV light was directed through a flow cell, which consisted of a Pyrex cross with fused-silica windows capping each arm. The UV beam propagated along the long arm of the cross, and fluorescence was collected perpendicular to the beam axis along the short arm. The fluorescence was passed through a polarization scrambler and was focused into a 1/4-m monochromator with a 1200 l/mm grating (Oriel). The light emerging from the monochromator was detected with a photomultiplier tube (PMT; Hamamatsu R955). The pulse energy of the UV beam was monitored both before and after the cell using pyroelectric detectors (Molelectron J3). The outputs of the PMT and pyroelectric detectors were digitized and stored on a computer, which also recorded the wavelength of the dye laser (LaserMetrics wavemeter) and the transmission of the dye laser through a monitor etalon (for linearization of the wavelength scale). The computer also controlled the scanning of the monochromator.

The flow cell could be evacuated to <100 mTorr using a mechanical pump. For these experiments, dilute SO₂ (1% in N₂) was introduced into the cell at a flow rate of 10-20 sccm. An additional flow of the bath gas (N₂ or O₂) could be introduced before the gases entered the cell. All flow rates were controlled by mass-flow controllers (MKS or Tylan). The pressure in the cell was regulated to 1.0-700 Torr by throttling the pump and was monitored using capacitance manometers (MKS).

To identify the most promising regions for LIF detection of SO₂, survey scans (absorption and fluorescence excitation) were recorded at UV wavelengths between 210.0 and 217.6 nm. These measurements indicated that the red end of this range is optimum for LIF detection (although the blue end would be preferable for absorption measurements). Higher resolution scans were recorded between 215.0 and 217.6 nm at several pressures using N₂ as the bath gas. Figure 1 shows example absorption and fluorescence-excitation spectra (the spectra at the different pressures have been off-set for clarity). Note the very different dependence on pressure of the different bands evident in these spectra. For instance, the band at ~216.5 nm has a lower absorption cross section than the band at ~217.0 nm (Fig. 1a), yet the two bands have a comparable fluorescence intensity at low pressure (Fig. 1b). Above 50 Torr, however, the fluorescence intensity of the ~216.5-nm band is much lower than that of the ~217-nm band. This behavior reflects the combined influences of the absorption cross section, emission cross section, nonradiative relaxation (predissociation), and collisional quenching on the fluorescence intensity and, ultimately, on the LIF detection sensitivity.

Based on the results of measurements such as those shown in Fig. 1, we performed high-resolution scans of the best regions for LIF detection of SO₂. These measurements indicated that the band at ~217 nm [α_2 (0,5)] is optimum for *in situ* LIF detection of SO₂

under conditions found throughout much of the atmosphere. This conclusion is based on the observation that this band has a relatively large absorption cross section and a large fluorescence quantum yield, even at elevated pressure. Moreover, the onset of this band (at 216.9 nm) is characterized by a sharp spike, providing a high on-line/off-line contrast ratio. Although this spectral feature is broadened at elevated pressures, the broadening is not prohibitive (on-line/off-line contrast ratio of 6/1 at 700 Torr), as seen in Fig. 1. Figure 2 shows high-resolution absorption and fluorescence-excitation spectra of this band at a pressure of 8.0 Torr.

Dispersed-fluorescence spectra were recorded for excitation at 216.9 nm and 215.2 nm. These spectra were recorded in the 200–400 nm region with a spectral resolution of 0.5 nm; they were corrected for the spectral response of the collection optics and detection system, which was measured using a calibrated deuterium lamp (Oriel). Figure 3 shows the dispersed-fluorescence spectra following excitation at 216.9 nm for three pressures (the spectra have been off-set for clarity). Although the dispersed-fluorescence spectrum broadens with increasing pressure, the spectrum does not shift, allowing the selection of an optimum detection wavelength and bandwidth that is not dependent on pressure. The fluorescence intensity decreases with increasing pressure (for a given SO₂ density) because of collisional quenching.

Laser Development

Development of a portable, LIF-based SO₂ sensor requires development of a compact source of tunable, narrow-bandwidth, UV radiation. Initial development of such a source was performed at the Naval Research Laboratory (Washington, DC). A Q-switched (pulsed), Yb-doped fiber laser pumped by a high-power diode laser (SDL) was built and tested. The gain medium consisted of a single-mode optical fiber whose core was doped with 2.5 wt.% Yb³⁺ ions (Polaroid). The core (mode-field diameter = 9.2 μm, NA = 0.08) was surrounded by a multimode cladding (100 x 200 μm, NA = 0.47), into which was launched ~200 mW of 974-nm pump radiation. The pump radiation was launched using a v-groove cut into the inner cladding near one end of the fiber [IEEE Photon. Technol. Lett. **10**, 793 (1998)], which allows compact and rugged packaging of the gain fiber and pump laser.

Figure 4 shows the laser system that was constructed using this gain fiber. One end of the fiber was connected to a Faraday mirror (a Faraday rotator and a retro-reflecting mirror). This device compensates for the birefringence of the fiber, which varies with thermal and mechanical fluctuations. In combination with the polarizing elements in the cavity, the Faraday mirror ensures stable, linear output polarization (important for nonlinear frequency conversion). A angle-tunable, dichroic filter (1060–1090 nm, 1.3 nm FWHM; DiCon) was positioned between the fiber and the Faraday mirror for wavelength selection and tuning; in future experiments, other wavelength-selecting elements (e.g., an etalon) will be incorporated into the cavity. The other end of the laser cavity consisted of a Pockels cell (to Q-switch the laser; LaserMetrics) between two polarizers; another Faraday rotator

maintained the correct polarization for the polarizers. Depending on the state of the Pockels cell, the output beam from the laser either passed out of the cavity or was reflected back into the fiber, as indicated in Fig. 4. Light was coupled into and out of the core of the Yb-doped fiber using FiberPorts (Optics for Research), which are compact and stable and are thus compatible with construction of rugged, portable instrumentation.

Qualitatively, the laser operates as follows: When the Pockels cell is “open” (i.e., set to pass light out of the cavity; dotted line in Fig. 4), the gain of the Yb-doped fiber increases until it reaches a maximum determined by the pumping rate and by amplified spontaneous emission (ASE). When the Pockels cell is “closed” (i.e., switched to recirculate the ASE), a pulse begins to build up in the laser cavity. This pulse is amplified on each pass through the fiber and is eventually dumped out of the cavity by re-opening the Pockels cell. The switching of the Pockels cell thus determines both the repetition rate of the laser system and the number of round-trip passes each pulse experiences (much like a regenerative amplifier). Quantitative simulations of the performance of this cavity were performed to aid in the design of the laser system.

The laser system produced pulses of 5-ns duration and up to 2.0 kW peak power at a repetition rate of 1-5 kHz. The results were in close accord with the numerical simulations. The power consumption (electrical) was <1 W. The UV wavelengths required for LIF detection of SO₂ (and NO) are accessible by frequency-quintupling of this source. Future experiments will entail further characterization and optimization of this new laser system and implementation of the nonlinear conversion scheme to generate tunable, UV light.

Fig. 1. Absorption (a) and fluorescence-excitation (b) spectra of SO₂ at the indicated pressures of N₂ bath gas.

Fig. 2. Absorption and fluorescence-excitation spectra of SO_2 at a pressure of 8.0 Torr (N_2 bath gas).

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Fig. 3. SO₂ dispersed-fluorescence spectra at various pressures (N₂ bath gas) following excitation at 216.9 nm. The first peak in each spectrum is laser scatter.

Fig. 4. Schematic diagram of the laser system. PBS = polarizing beam splitter, M = mirror, FR = Faraday rotator, FP = FiberPort., λ = tunable filter.

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