In Situ Measurement of Tropospheric OH Radicals by Laser-Induced Fluorescence—
A Description of the KFA Instrument

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ABSTRACT

An instrument for the measurement of tropospheric OH radical concentrations by laser-induced fluorescence spectroscopy has been developed. Ambient air is expanded through a nozzle into a low-pressure fluorescence cell and is irradiated by a frequency-doubled dye laser, which is pulsed with a high repetition rate of 8.5 kHz. The laser wavelength is tunable to selectively excite single rovibrational transitions of the OH radicals at 308 nm $[A^2Σ^+ (v' = 0) - X^2Π (v'' = 0)]$. The OH resonance fluorescence, emitted mostly between 307 and 311 nm, is detected by gated photon counting. From laboratory calibrations and ambient air measurements the authors infer a detection limit $(S/N = 2)$ of $8 \times 10^7$ OH cm$^{-3}$ for 1-minute data integration time. First tests of the new instrument in ambient air revealed the existence of an interference problem due to generation of OH by a dark reaction of ozone inside the detection cell. Improvements of the instrument reduced the spurious OH signal to a level corresponding to an ambient OH concentration of $3 \times 10^3$ cm$^{-3}$, thus being within the detection limit of the instrument. During a sunny and clear period in May–June 1994 the instrument was tested in the field. For the first time it was possible to record excitation spectra of tropospheric OH comprising the $Q_1(3)$, $Q_2(3)$, and $P_1(1)$ rotational lines. The analysis of the data yielded hydroxyl radical concentrations of up to $4 \times 10^6$ molecules cm$^{-3}$. These spectra unambiguously identify the OH radical and demonstrate the high detection sensitivity and selectivity of this new instrument.

1. Introduction

Hydroxyl (OH) radicals play a key role in tropospheric photochemistry (Ehhalt et al. 1991). The hydroxyl radical is the primary atmospheric oxidant and controls the chemical lifetime of most natural and anthropogenic trace gases. The dominant tropospheric source of OH radicals is the reaction of H$_2$O with O(’D) atoms, which are formed by photolysis of ozone with solar radiation at wavelengths less than 320 nm. The chemical reactions of OH with trace gases initiate radical chain reactions, which mostly lead to the formation of hydroperoxy (HO$_2$) radicals as an intermediate. Over regions like middle Europe, where the daytime concentrations of NO exceed 0.1 ppb, HO$_2$ is quickly recycled to OH predominantly by reaction with NO. This and the fact that OH does not react with the main constituents of the atmosphere establish the prominent role the radical plays in the decomposition process of tropospheric trace gases.

In order to test current tropospheric photochemical models, it is desirable to measure atmospheric OH concentrations with a temporal resolution on the order of 1 minute. This timescale reflects the high variability of the OH concentration, which quickly follows any changes of the physical and chemical parameters determining its production, interconversion via HO$_2$, and loss (e.g., see Poppe et al. 1993). Since the abundance of this short-lived radical is extremely low—only about some $10^6$ molecules cm$^{-3}$ for typical midday conditions—a highly sensitive detection technique is needed. Laser-induced fluorescence (LIF) spectroscopy is a method capable of making local in situ measurements of atmospheric OH at such extremely low concentrations.

The detection of OH radicals in the troposphere by laser-induced fluorescence spectroscopy is usually based on its strong discrete line absorption spectrum $\left( A^2Σ^+ (v' = 0) \leftrightarrow X^2Π (v'' = 0) \right)$ around 308 nm. Hydroxyl radicals can be selectively excited by a narrow-bandwidth laser (excitation spectroscopy). The amount of resonant fluorescence light subsequently emitted by excited OH radicals (OH$^*$) at 307–311 nm can be used as a measure for the OH concentration.

All current LIF systems used for OH detection in the troposphere (Chan et al. 1990; Hofzumahaus and Holland 1993; Hofzumahaus et al. 1994; Stevens et al. 1994) utilize the fluorescence assay with gas expansion (FAGE) concept first developed by Hard et al. (1984). Ambient air is expanded through a nozzle into a low
pressure (1–5 mbar) fluorescence chamber. The OH radicals are detected directly in the gas beam formed. The low pressure offers the advantage of greatly reducing laser-excited background signals (Rayleigh and Mie scattering), whereas the OH signal is only slightly diminished (Hard et al. 1984; Hofzumahaus and Holland 1993; Stevens et al. 1994).

In this paper we describe our LIF instrument, which is based on a high repetition rate (8.5 kHz) laser system, that has sufficient sensitivity to detect ambient OH concentrations of about $8 \times 10^5$ cm$^{-3}$ with a S/N = 2 in 1 min. The characteristics of an interference due to generation of OH in our fluorescence cell encountered in the presence of ozone are discussed. Calibration and ambient air measurements are presented. This instrument expands and complements the OH measurement capabilities of our institute already provided by the laser long-path absorption spectroscopy technique (Dorn et al. 1994).

2. Experimental

A diagram of the LIF instrument is shown in Fig. 1. The major parts of the instrument are 1) the laser system, 2) the OH fluorescence cell, 3) the detector, 4) the wavelength reference, and 5) the data acquisition system.

**Laser system.** A grating-tuned, pulsed dye laser (Lambda Physik LPD 3002) is pumped by a high repetition rate (8.5 kHz) copper vapor laser (CVL) (Oxford Lasers ACL 35, equipped with an unstable cavity). The pump power of the CVL ranges from 19 to 27 W depending on the usage of the copper load. The dye solution is a mixture of Rhodamin 590 (Lambda Physik, 0.15 g L$^{-1}$) and Rhodamin 640 (Lambda Physik, 0.10 g L$^{-1}$) in methanol (Riedel-de Haën, p.a.), which is optimized to yield a maximum output at 616 nm using both laser wavelengths (511 and 578 nm) of the CVL. However, the chemical stability of the mixture is poor. Within about 25 h of operation the 616 nm output power decreases by a factor of 2. The dye laser output is frequency doubled using a BBO crystal to yield up to 300 mW (35 $\mu$J/pulse) of 308-nm radiation with a pulse length of 12 ns and a spectral bandwidth of 6 GHz. A set of Pellin-Broca prisms separates the UV output from the red fundamental radiation. The beam passes through a combination of a λ/2 plate and a Glan Thompson polarizer, which allows for a continuous attenuation of the laser light without changing the plane of polarization. A cylindrical and a spherical beam-expanding telescope are needed to produce a beam with a circular shape of about 8-mm diameter. The laser beam enters and leaves the fluorescence cell through a series of light baffles, which shield the detector against sun light and fluorescent light from the entrance and exit windows. The laser fluence inside the cell is kept low (typically 10 $\mu$J cm$^{-2}$) to keep saturation of the strong rovibronic OH transitions [Q$_1$(2), Q$_1$(3), or P$_1$(1) line] below 10%.

**Fluorescence cell.** The fluorescence cell is a cube made out of aluminum that is anodized black in order to reduce stray light. Ambient air is expanded through a nozzle (Beam Dynamics Inc.; orifice diameter of 0.75 mm, material: nickel, flow rate of 60 mbar L s$^{-1}$) into

![Fig. 1. Schematic of the LIF instrument: components are PD: photodiode, GTP: Glan–Thompson polarizer, AH: aperture hole, M: mirror, BS: beam splitter, A: amplifier, PA: preamplifier, PMT: photomultiplier tube, DG: dynode gating driver, HV: high voltage supply, GPC: gated photon counter, and ADC: analog-to-digital converter.]
the chamber maintained at 1 mbar by a vacuum pump (Edwards QMB 500/QDP 80, not depicted in Fig. 1). The gas expansion produces a fast (200 m s\(^{-1}\)) collimated gas beam of about 8-mm diameter in the detection volume, which does not experience wall collisions except in the nozzle orifice. To avoid buildup of gaseous contaminations in the baffle arms, dry nitrogen is added close to the windows flowing toward the center of the cell with a flow rate of 3 mbar L s\(^{-1}\).

Detector. The gas beam is crossed by the laser beam at right angles. Perpendicular to this plane, a fused silica condenser (f # = 1) with a narrowband interference filter (Omega, \(\lambda_{\text{center}} = 310 \text{ nm}, T = 32\%\), FWHM = 9 nm) and an additional solar-blind filter (Corion, SB 300, \(T = 70\%\)) is mounted outside the cell to image the OH-fluorescence light onto a photomultiplier (PMT) (EMI 9815QB). On the opposite side of the fluorescence chamber a concave mirror is placed, doubling the solid angle seen by the PMT. The PMT pulses (FWHM = 3 ns, mean amplitude = -35 mV) pass through a 10-cm coax cable into a 300-MHz preamplifier (Stanford Research Systems SR445) with a gain of 5. The amplified signals are fed into a 200-MHz gated photon counter (Stanford Research Systems SR400), which is equipped with a 10-dB attenuator (Suhner) to adopt the signal amplitude to the working range of the discriminator.

Although the fluorescence cell is kept at a low pressure of 1 mbar, each laser pulse generates an intensive stray-light pulse mainly due to Rayleigh and Mie scattering. This short-lived signal (308 nm, 12 ns duration) is separated from the much weaker longer-lived OH fluorescence (307–311 nm, about 320-nm lifetime) by delayed photon counting (temporal filtering). The counter gate has a delay of 250 ns with respect to the laser pulse and a width of 500 ns. In addition, the gain of the photomultiplier is switched off while the PMT is exposed to the initial laser stray-light pulse. This way gain saturation is avoided and photomultiplier afterpulsing is strongly reduced. The laser power is continuously measured by calibrated photodiodes. For normalization the counted photons accumulated in 1 s are divided by the laser power averaged over 1 s (see below).

Wavelength reference. A second fluorescence cell is set up to provide an OH wavelength reference. Hydroxyl radicals are produced by photolysis of water vapor in a slow flow of argon using the 185-nm radiation of a low-pressure mercury lamp. The pressure in the cell is kept at 200 mbar, which was found to yield the highest OH signal with the best signal to noise ratio. The fluorescence photons are detected by gated photon counting. The signal is monitored in parallel to the ambient air measurement.

Data acquisition system. The amplified photodiode signals as well as other experimental parameters (e.g., pressure in the fluorescence cell, humidity and ozone mixing ratios for calibration measurements, flow rates, ozone photolysis frequency for ambient measurements, etc.) are permanently monitored and averaged over a period of 1 s by a data acquisition system (Keithley, Series 576). The time base of the system is determined by one of the photon counters, which accumulates the photomultiplier signals for 1 second and then triggers the readout of the photon counters and the data acquisition system. Averaging of the data over any number of readouts can be selected in the software package used to run the system. The dye laser, photon counters, and data acquisition system are controlled by a PC via an IEEE interface. The whole LIF instrument can accumulate data automatically for several hours.

3. Sensitivity and detection limit

Laser-induced fluorescence spectroscopy is a direct detection method. The relationship between the number of fluorescence photons counted per second, \(S_{\text{OH}}\) (in cts s\(^{-1}\), where cts = counts), the corresponding OH concentration [OH] (in molecules cm\(^{-3}\)), and the laser power \(P\) (in mW) is given by

\[
S_{\text{OH}} = \frac{\text{accumulated counted photons}}{\text{integration time}} = C \cdot P \cdot [\text{OH}],
\]

where \(C\) is the sensitivity of the instrument (in cts s\(^{-1}\) mW\(^{-1}\)/(OH cm\(^{-3}\))), which depends on specific experimental parameters as well as general spectroscopic properties of the OH radical. Based on the notation of Stevens et al. (1994), the sensitivity can be expressed as

\[
C = \frac{B_{12}}{\varepsilon^2} \left( \frac{4 \ln 2}{\pi} \right)^{1/2} \cdot (\Delta \nu_\text{D}^2 + \Delta \nu_\text{I}^2)^{-1/2} \cdot \frac{\Delta N}{N} \cdot \frac{4}{\rho_{\text{amb}}} \gamma_{\text{ampling}},
\]

where

\[
\gamma_{\text{ampling}} = \exp \left( -\frac{\Delta T_e}{\tau} \right) - \exp \left( -\frac{\Delta T_e + T_e}{\tau} \right)
\]

and

\[
Q = \frac{\tau}{\tau_{\text{rad}}},
\]

with

\[
\tau = \left( \tau_{\text{rad}}^{-1} + k_q[M]^{-1} \right)^{-1}
\]

\[
B_{12} \quad \text{Einstein B-coefficient for absorption}
\]

\[
\Delta \nu_\text{D} \quad \text{OH Doppler and laser line widths, respectively}
\]

\[
\Delta N/N \quad \text{fraction of OH molecules in the rotational level being excited}
\]

\[
l \quad \text{length of the laser beam overlapping the ambient airstream}
\]
The set of parameters applying to our current setup of the instrument is listed in Table 1. However, the sensitivity determined from Eq. (2) is only an estimate since the calculation involves some parameters that are not easily accessible by measurements or calculations. This is especially true for the excitation length, the collection efficiency of the optics, and the sampling efficiency for OH radicals. A calibration of the absolute sensitivity is therefore necessary. For that reason we have developed a calibration source that provides known concentrations of OH radicals in air for nearly atmospheric conditions. Since the experimental setup has been described in detail elsewhere (Aschmutat et al. 1994), only a brief outline will be given here. We use a laminar flow tube with its outlet set up in front of the inlet nozzle of the fluorescence chamber. A constant flow of synthetic air with a known amount of water vapor (10–1000 ppm) is passed through the tube at 1 atm. Irradiation of the gas with 185-nm radiation from a low-pressure mercury lamp photodissociates H$_2$O molecules into OH radicals and H atoms. The intensity of the lamp is monitored by the amount of ozone produced photolytically in parallel with the OH radicals. Hydroxyl radical concentrations can be controlled between about 3 x 10$^6$ molecules cm$^{-3}$ and 3 x 10$^9$ molecules cm$^{-3}$. The precision of the method, which is estimated to be 14%, is limited by the precision of the ozone measurement. The accuracy, which is mainly determined by uncertainties associated with the absorption cross sections of H$_2$O and O$_2$, is about 40%.

Here, for the calibration of the instrument OH concentrations between 5 x 10$^6$ cm$^{-3}$ and 7 x 10$^7$ cm$^{-3}$ were used. The data obtained from an evaluation of the $P_i(1)$ and $Q_i(3)$ lines are plotted in Fig. 2. The OH signal was found to vary linearly with the radical concentration. From this relationship detection sensitivities $C$ of 1.0 x 10$^{-7}$ cts s$^{-1}$ mW$^{-1}$/((OH cm$^{-3}$) for the $Q_i(3)$ transition and of 1.3 x 10$^{-7}$ cts s$^{-1}$ mW$^{-1}$/((OH cm$^{-3}$) for the $P_i(1)$ transition were derived for OH detection in synthetic air containing only traces of water vapor. In moist ambient air the sensitivity is expected to be reduced due to quenching of the OH fluorescence by water molecules. For our experimental conditions the reduction calculated from known quenching cross sections (Copeland et al. 1985; Kenner et al. 1990) is small, about 10% for a water

<table>
<thead>
<tr>
<th>$B_i$(cm$^3$ s$^{-1}$), $Q_i(3)$:</th>
<th>$P_i(1)$:</th>
<th>Dimpfle and Kinsey 1979</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.01 x 10$^{24}$</td>
<td>0.76 x 10$^{24}$</td>
<td>Calculated</td>
</tr>
</tbody>
</table>

| $\Delta \nu_0$ (cm$^{-1}$) | 0.10      | Measured            |
| $\Delta \nu_i$ (cm$^{-1}$) | 0.20      | Calculated          |
| $\Delta N/N$ at $T = 207$ K | 0.071 | Measured            |
| $Q_i(3)$:                   | 0.145     | Calculated          |
| $P_i(1)$:                   | 0.36      | Measured            |
| $Q_i(3)$:                   | 0.35      | Calculated          |
| $P_i(1)$:                   | 250       | Calculated          |
| $T_i$ (ns):                 | 500       | Measured            |
| $\tau$ (ns), $Q_i(3)$:     | 320       | Measured            |
| $P_i(1)$:                   | 290       | Calculated          |
| $Q_i(3)$:                   | 0.47      | Measured            |
| $P_i(1)$:                   | 0.42      | Calculated          |
| $\tau_{rad}$ (ns)          | 688       | Measured            |
| $\rho_{in}/\rho_{amb}$     | 0.0010    | Measured            |
| $\gamma_{sampling}$         | 1         | Calculated          |

$C$ [cts s$^{-1}$ mW$^{-1}$/((OH cm$^{-3}$)]

$Q_i(3)$: 2.1 x 10$^{-7}$

$P_i(1)$: 2.8 x 10$^{-7}$

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Table 1. Estimation of the sensitivity of OH detection from experimental parameters of the KFA-LIF system as determined from Eqs. (2)–(5).
vapor mixing ratio of 1% (about 50% relative humidity at 20°C). Recent measurements in our laboratory of the fluorescence lifetime of OH* as a function of the water vapor concentration suggest that this dependence may be even smaller (see below). Compared to the calibrated sensitivity, the estimated value from Eq. (2) is larger by a factor of 2. However, in view of the uncertainties connected with some of the parameters in Table 1 this discrepancy is acceptable.

The background limited detection limit \([\text{OH}]_{\text{min}}\) of the instrument at a certain signal to noise ratio, \(S/N\), is related to the sensitivity \(C\) by

\[
[\text{OH}]_{\text{min}} = \frac{S}{N} \cdot \frac{1}{C \cdot P} \sqrt{\frac{1}{m} + \frac{1}{n} \cdot \sigma_b}
\] (6)

with

- \(P\) laser power (in mW),
- \(\sigma_b\) sample standard deviation of the background signal (in cts s\(^{-1}\)),
- \(m\) number of OH measurement (on resonance),
- \(n\) number of background measurement (off resonance).

If the distribution of the background signals follows Poisson statistics, its sample standard deviation is given by

\[
\sigma_b = \sqrt{\frac{1}{t} (S_{sb} + S_{sb} + S_{sb})}
\] (7)

with

- \(S_{sb}\) laser-induced background signal (in cts s\(^{-1}\)),
- \(S_{sb}\) solar stray-light background signal (in cts s\(^{-1}\)),
- \(S_{sb}\) dark signal of the photomultiplier (in cts s\(^{-1}\)),
- \(t\) data accumulation time per wavelength position (in seconds).

During a field test, the laser-excited background signal \(S_{sb}\) was determined to be 23 cts s\(^{-1}\) at a laser power of 40 mW. An additional contribution, \(S_{sb}\), of up to 50 cts s\(^{-1}\) was caused by solar stray light entering the fluorescence chamber through the nozzle. The dark signal of the photomultiplier was negligible. The solar stray-light contribution was measured separately on a pulse-to-pulse basis taking advantage of the photon counter to internally split the PMT signal and feed it into two independently configurable counterchannels. While the fluorescence photons are captured with a 500-ns gate following 250 ns after the laser pulse, the solar stray-light channel utilizes a gate with a delay and width of 25 \(\mu\)s and 50 \(\mu\)s, respectively. One hundredth of the latter count rate is subtracted from the fluorescence measurement every second when the two counter channels are read out by the data acquisition software. Due to the one hundred times longer gating time of the solar stray-light channel, these measurements have a high precision and contribute to only 1% to the imprecision of the fluorescence measurement.

For a two-point measurement \((n = m = 1)\) using the \(P_{1}(1)\) transition of OH, Eqs. (6) and (7) yield a detection limit of about \(8 \times 10^5\) OH cm\(^{-3}\) for 30 seconds of data integration time on- and off-resonance each (S/
N = 2, P = 40 mW, S_{th} = 23 cts s^{-1}, S_{ab} = 50 cts s^{-1}, S_{sb} = 0 cts s^{-1}).

4. Interferences

The detection of ambient OH radicals by laser-induced fluorescence can be effected by different types of interferences. The most prominent interference in the early attempts to measure tropospheric OH concentrations using excitation at 282 nm was the self-production of OH radicals in the detection chamber by photolysis of ambient ozone by the laser radiation and subsequent reaction of the O(1D) atoms with water vapor [e.g., Smith and Crosley (1990) and literature cited therein]. In order to overcome this problem new OH detection techniques were developed that use laser excitation at a wavelength of 308 nm (Chan et al. 1990; Hofzumahaus et al. 1990; Stevens et al. 1994). At this wavelength the photodissociation cross section of ozone is smaller by a factor of 31 (Molina and Molina 1986; JPL 1992). At the same time the absorption cross section of OH is larger by a factor of 3.95 (Chidsey and Crosley 1980); thus less laser pulse energy is required to obtain the same OH detection sensitivity. Therefore, the photolytic production of OH in the fluorescence cell is smaller by a factor of ~120. Indeed, measurements reported by Stevens et al. (1994) showed that for their system the ozone—water interference was below their detection limit of about 1 x 10^{3} cm^{-3} (for 300 ppb ozone and 3% water).

In contrast, we became aware of a new interference problem during the first ambient air measurements with our own instrument. Hydroxyl radical signals were observed equivalent to ambient OH concentrations of about 3 x 10^{5} cm^{-3}. The measurements, however, did not show the expected dependence on the ozone photolysis frequency J(O1D). Laboratory tests revealed that OH radicals were produced in our fluorescence cell in the presence of ozone. Due to the reduced pressure in the cell, the extremely small concentration of some 10^{3} OH cm^{-3} is sufficient to account for the interference observed. The signal showed a linear dependence on the ozone concentration. However, different from the “classic” photolytic ozone—water interference, the signal did not depend on the water vapor mixing ratio and exhibited a linear dependence on the pulse energy. The latter finding excludes the possibility of a photolytic production pathway of the OH radicals unless one of the two photolytic steps involved in the detection process is saturated. This possibility, however, can be ruled out since the laser pulse fluence in our experiment is far too small (<=10 μJ cm^{-2}) to significantly saturate either the ozone or the OH absorption transition.

Although we have not yet fully identified the processes responsible for the OH generation, we have strong evidence to draw the conclusion that the artificial OH is not formed in the gas beam but is produced by a dark reaction, either in the background gas phase by an unknown reaction or on the walls of our cell. The different origin of the OH radicals sampled by the nozzle and the OH generated in our cell becomes apparent from a comparison of the corresponding spectra shown in Figs. 3a and 3b. The ratio of the line intensities of the P_{1}(1) and Q_{1}(3) rovibronic transitions in spectrum (a) is characteristic of OH radicals seeded in the gas beam, which experience rotational cooling in the adiabatic expansion. In contrast, spectrum (b), which was obtained from the interference OH, shows the line intensity pattern expected for OH molecules being in a thermal equilibrium at room temperature.

To reduce the amount of OH produced we tested different cell coatings, black paint (3M), black and white Teflon, and black anodized aluminum, and found

![Excitation spectra of OH measured with the same instrumental setup but (a, b) without and (c, d) with an additional aperture hole installed in the detection optics (see text); (a, c) OH radicals in synthetic air expanded through the nozzle ([OH] = 1.2 x 10^{6} cm^{-3}, data integration time: 5 s, laser power: 30 mW) and (b, d) OH radicals produced by an unknown mechanism inside the fluorescence cell in the presence of 950 ppb ozone [data integration time: 10 s (b), 20 s (d), laser power: 30 mW]. Symbols denote measurements; the solid lines display five-point running averages of the observed data.](image-url)
the latter material to be the most appropriate one. A higher volume flow through the nozzle, which was established by increasing the diameter from 0.29 to 0.75 mm, helped to reduce the artificial OH concentration in the detection zone. Figures 3c and 3d show the result of a reduction of the field of view of the PMT with an additional aperture hole mounted at the focus of the condenser system. This measure prevents the detector from seeing parts of the laser beam that do not intersect with the gas beam and are therefore the prominent source of interference OH fluorescence signals. With these improvements a considerable reduction of the interference signal was obtained. A spectrum measured in the presence of 100 ppb ozone and with an accumulation time of 100 s per data point showed no interference signal anymore. A detection limit of $3 \times 10^5$ OH cm$^{-2}$ for $S/N = 2$ was inferred from the noise in the spectrum.

5. Atmospheric measurements

During a period of sunny and clear days in May and June 1994 we made atmospheric measurements with our improved instrument just outside the building of our institute in Jülich. Starting around noon on 31 May, 23 spectra covering the Q$_1$(3), Q$_{21}$(3), and P$_1$(1) lines of OH were recorded until the late afternoon of 1 June. This was the first time excitation spectra in the (0-0) band of the A–X system of tropospheric OH radicals have been observed. With an integration time of 30 s per data point and a wavelength increment corresponding to 1 GHz, the scan of each spectrum took about 50 min. During daytime we observed OH signals of varying strength, which approximately follow the ozone photolysis frequency $J$(O'D) measured with a filter radiometer mounted just beside our LIF instrument.

Figure 4 shows two spectra of ambient air recorded during the measurement period and a reference spectrum for comparison. The open diamonds mark the original data, which, for better comparability, were normalized to the laser power (i.e., counts accumulated in 30 s per mW$^{-1}$ of laser power). The solid line shows a five-point running average of the original data. The spectrum with the highest OH signal observed is depicted in Fig. 4b. With the calibration factors given in Fig. 2, OH concentrations of $3.3 \times 10^8$ cm$^{-3}$ and $3.4 \times 10^8$ cm$^{-3}$ are inferred from the Q$_1$(3) and P$_1$(1) line, respectively. The spectrum was measured in the early afternoon of 1 June. The time period covered by this measurement was characterized by stable conditions for the ozone mixing ratio, $J$(O'D), relative humidity, temperature, and hence the expected OH production rate. The intensities of the two prominent lines, Q$_1$(3) and P$_1$(1), reflect the pattern typical of rotationally cold OH radicals. This spectrum clearly identifies OH in the ambient air. Different from laser long-path absorption measurements in the polluted air of Jülich where the OH structure is blended by much stronger absorptions due to SO$_2$, formaldehyde, and naphthalene the excitation spectrum solely exhibits spectral lines of the hydroxyl radical. The spectrum shown in Fig. 4a was observed in the early evening of 31 May. While the ozone mixing ratio was still above 50 ppb, $J$(O'D) had dropped to $10^{-7}$ s$^{-1}$. Based on Eq. (6) the noise in the spectrum, which does not show any absorption lines, puts an upper limit on the OH concentration of $\approx 6 \times 10^3$ cm$^{-3}$ ($S/N = 2$, $P = 33$ mW, $m = 1$, and $n = 100$). This value is in agreement with a detection limit of $4 \times 10^5$ OH cm$^{-3}$, which can be calculated using Eq. (7), which assumes that the noise in the spectrum is determined by Poisson statistics ($S_{th} = 20$ cts s$^{-1}$, $S_{sb} = 0$ cts s$^{-1}$, $S_{db} = 0$ cts s$^{-1}$, and $t = 30$ s).

Compared to the spectrum observed in the afternoon the background signal in the evening spectrum has risen, an observation which became much more prominent later at night and early in the morning when temperatures had dropped to a minimum and the relative humidity reached levels above 92%. Since the adiabatic expansion lowers the temperature of the gas, we attribute the increase of the background signal to an increasing stray-light pulse caused by water droplets formed in the expanding gas beam, a process that becomes more favorable when temperatures are low and humidity is high. A visible sign of the cooling process was the condensation of water droplets and finally the formation of an ice cap around the tip of the nozzle during the nighttime hours of our field measurement.

This interpretation gets further support from recent measurements in our laboratory of the fluorescence lifetime $\tau$ of OH* ($A^3\Sigma^+$, $v = 0$) as a function of the water vapor concentration. Since H$_2$O is an efficient quencher for OH*, one would expect a decreasing lifetime as [H$_2$O] increases. However, the measurements have shown that $\tau$ is independent of [H$_2$O] for water vapor mixing ratios between 0.2 and 1.6%. This can be interpreted in terms of a constant water vapor concentration in the gas phase determined only by the number density and temperature of the expanding gas beam. The excess water is removed from the gas phase via the formation of droplets.

This consideration sheds some light on the important question of the possibility of clustering of OH radicals with water molecules in the expanding gas beam. These radicals would become effectively invisible to the measurement since their rovibrionic transition frequencies will be shifted to the red. Therefore, the evaluation of ambient air measurements based on our present calibration technique with only traces of water could yield OH concentrations systematically too low. However, at present we do not have enough information to quantify this possible loss of sensitivity of our instrument.

6. Conclusions

We have developed a highly sensitive instrument for the measurement of tropospheric OH radical concen-
FIG. 4. (a) Spectrum of ambient air measured on 31 May 1994 from 1954 to 2047 LST: [OH] \( \leq 6 \times 10^3 \text{ cm}^{-3} \), \( J(\text{O}^\text{D}) \leq 10^{-7} \text{ s}^{-1} \), \( x(\text{O}_3) = 51 \text{ ppb} \), \( x(\text{SO}_2) = 13 \text{ ppb} \), \( x(\text{CH}_3\text{O}) = 6 \text{ ppb} \), \( x(\text{C}_3\text{H}_6) = 66 \text{ ppt} \), RH = 43%, \( T = 19^\circ \text{C} \), \( P = 33 \text{ mW} \). (b) Spectrum of ambient air measured from 1504 to 1558 LST 1 June 1994: \( [\text{OH}] = 3.4 \times 10^4 \text{ cm}^{-3} \), \( J(\text{O}^\text{D}) = 9 \times 10^{-7} \text{ s}^{-1} \), \( x(\text{O}_3) = 57 \text{ ppb} \), \( x(\text{SO}_2) = 4 \text{ ppb} \), \( x(\text{CH}_3\text{O}) = 8 \text{ ppb} \), \( x(\text{C}_3\text{H}_6) = 35 \text{ ppt} \), RH = 25%, \( T = 29^\circ \text{C} \), \( P = 26 \text{ mW} \). (c) OH reference spectrum simultaneously measured in the reference cell at room temperature. The integration time per data point was 30 s. Symbols denote measurements; the solid lines display five-point running averages of the observed data.

trations by pulsed laser-induced fluorescence spectroscopy at low pressure. Laboratory calibration has shown that the sensitivity of the instrument is sufficient for measurements of tropospheric OH concentrations within one minute of data integration time. During first ambient air measurements the appearance of a spurious OH signal was encountered in the presence of ozone. From its characteristics we deduce that the OH is generated in a nonphotolytic process inside our detection chamber, probably on the walls of the cell. Improvements on the optical train imaging the fluorescence volume onto the photomultiplier helped to reduce the interference signal below a corresponding ambient OH concentration of about \( 3 \times 10^5 \text{ cm}^{-3} \). However, more work is needed to arrive at a comprehensive understanding of the mechanisms underlying this dark OH source. Other improvements of the instrument, like flushing the walls of the fluorescence cell with dry nitrogen, are in progress. A further reduction of the interference signal is essential since we plan to reduce the detection limit of our instrument.

Recent atmospheric measurements demonstrated the capability of our instrument to obtain excitation spectra of tropospheric OH radicals. These spectra unambiguously identified OH as the source of the fluorescence signal observed and proved the selectivity of the tech-
nique with respect to potential interferences due to other molecules absorbing light in the spectral region under investigation. To increase the time resolution we can switch to a two-point measurement mode (on- and off-resonance with an OH absorption line), which will then provide OH data on a one minute basis.

The instrument is now going to be tested extensively in the field. In particular, we will carry out an informal instrumental intercomparison by simultaneous in situ measurements of OH using LIF and laser long-path absorption spectroscopy that utilizes a multiple folded light path (Dorn et al. 1995). These measurements will be part of the POPCORN (Photo-Oxidant Formation by Plant Emitted Compounds and OH Radicals in North-Eastern Germany) field campaign, which will take place in August 1994.

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REFERENCES


