The Measurement of Tropospheric Trace Gases at Fritz Peak Observatory, Colorado, by Long-Path Absorption: OH and Ancillary Gases

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ABSTRACT

The determination of the concentration of the hydroxyl radical in the troposphere is of fundamental importance to an understanding of the chemistry of the lower atmosphere. Described here are experiments located at Fritz Peak Observatory, Colorado, that measure the OH concentration to a sensitivity limit of about $5 \times 10^3$ cm$^{-3}$ (0.025 pptv) with absolute error approximately ±30% and, simultaneously, measure the concentrations of H$_2$O, SO$_2$, CH$_3$O, NO$_2$, NO, HONO, O$_3$, and other trace gases in the troposphere that affect OH concentration to provide a test of photochemical theories of OH formation and destruction. An informal OH intercomparison campaign that occurred at Fritz Peak in 1991 and the 1993 Tropospheric OH Photochemistry Experiment are discussed.

1. Introduction

The hydroxyl radical (OH) plays a central role in the chemistry of the earth's lower and middle atmosphere. The determination of its concentration is essential since this molecule controls the lifetimes, and therefore the concentrations, of many chemical species under both clean and polluted conditions. Midlatitude predicted concentrations of OH range from about 0.1 pptv at noon in the winter to 0.5 pptv at noon time in the summer. These low values are extremely difficult to measure.

The importance of the OH molecule in tropospheric chemistry was first recognized in the late 1960s (Weinstock 1969; Levy 1971). Since that time, a number of experiments have been made to determine its concentration in the troposphere (Davis et al. 1976; Wang et al. 1976; Bakalyar et al. 1982; Hubler et al. 1984; Rodgers et al. 1985; Hard et al. 1986; Campbell et al. 1979; Shirinzadeh et al. 1987; Perner et al. 1987; Platt et al. 1988; Dorn et al. 1988; Eisele and Tanner 1991; Ehhalt et al. 1991; Mount 1992; Eisele and Tanner 1993; Poppe et al. 1993; Poppe et al. 1994; Tanner and Eisele 1995). These measurements have produced mixed results with recent sensitivity limits as low as $1 \times 10^3$ cm$^{-3}$. Tropospheric measurements are extremely difficult, and most of the experiments have suffered from considerable uncertainty (Ortgies et al. 1980; Davis et al. 1981a,b). Many of the measurements performed in the past 20 years have been exploratory in nature and have not provided a rigorous test of the photochemical theories.

Recent work by the NOAA Aeronomy Laboratory and Georgia Institute of Technology groups have shown that the OH concentrations are significantly lower than predicted by most models (Mount and Eisele 1992; Eisele et al. 1994). The results of the measurements performed to date by these two groups indicate that the noontime concentration of the OH radical in the clean [NO$_x$ < 200 parts per trillion volume (ppbv)] and clear troposphere varies at noon between approximately 2 and 3 ($\times 10^5$ cm$^{-3}$) for summertime conditions as measured in a forested environment. An informal campaign to determine tropospheric hydroxyl concentration and intercompare two OH instruments was conducted at Fritz Peak Observatory, Colorado, from 15 July to 24 August 1991 (Mount and Eisele 1992; Eisele et al. 1994). These measurements provide a stringent test of the ability to measure OH concentrations since these instruments use completely different measurement techniques. Hydroxyl concentrations on all days were found to be significantly lower than model predictions, indicating the possible presence of a scavenger. The measured OH concentrations from the two experiments compared well in both clean and polluted air masses throughout the measurement period with few exceptions. The 1991 intercomparison showed that ambient OH concentrations can now be measured with sufficient sensitivity to provide a rigorous test for photochemical models.

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A new Tropospheric OH Photochemistry Experiment (TOHPE) with many more participants (Table 1) measuring many more species that affect the OH concentration and therefore giving a much more comprehensive picture of the OH photochemistry was completed at Fritz Peak in Fall 1993. The campaign ran from mid-August through September 1993 and covered periods of warm, clear weather and periods of snowy weather, which removed the biogenic hydrocarbons from the local atmosphere. Thousands of OH data points were acquired, and low OH concentrations were once again measured under clean conditions.

The theoretical aspects of OH tropospheric chemistry have been thoroughly studied, and OH chemistry has been placed in the framework of the global troposphere (Logan et al. 1981; Perner et al. 1987). Atmospheric OH is formed (mainly) by reaction of \( O^1(\text{D}) \) with water vapor:

\[
O_3 + hv \rightarrow O_2(1\Delta g) + O^1(\text{D}) \quad (\nu < 310 \text{ nm}).
\]

(1)

Up to 10% of the \( O^1(\text{D}) \) in the planetary boundary layer reacts with water vapor to give OH:

\[
O^1(\text{D}) + H_2O \rightarrow OH + OH.
\]

(2)

Excellent summaries of the reactions and rate constants used for theoretical calculation of tropospheric OH chemistry are available (e.g., Perner et al. 1987).

2. Experiment description: OH

Figure 1 shows the basic layout used in our long path OH experiment. A laser light source is collimated and passed through the atmosphere over a 10.3-km path. At the end of the path a 121-element retroreflector array is located to return the light beam back to its origin at Fritz Peak where a receiver telescope focuses it onto the entrance slit of a spectrograph with a sophisticated array detector, which allows simultaneous viewing of the requisite spectral region. The experimental apparatus consists of six basic components: 1) a spectrally bright (tens of milliequivalents) pulsed ultraviolet laser light source with optics for directing a low divergence light beam into ambient air outside the observatory, 2) a mirror system located 10.3 km distant to collect the light beam and return it to the observatory for a total absorption pathlength of 20.6 km, 3) a telescope collector located in the laboratory at the observatory, 4) a very high resolution (resolving power \( > 500 \ 000 \)) dual-channel spectrograph to allow accurate spectral resolution of individual rotational lines in the ultraviolet electronic OH bands near 308 nm, 5) a two-channel array detector system that allows simultaneous observation of a spectral interval sufficient to include several OH rotational lines on both the reference channel and the absorbed channel, and 6) a data collector/analysis system that allows computer control of the hardware.

The basic physics of the experiment has been presented elsewhere (Hubler et al. 1984). To summarize, concentration of OH is determined from differential absorption according to the Lambert–Beer law:

\[
\ln(l/l_0) = -\sigma[OH]L(n/n_0),
\]

(3)

at each wavelength and where

- \( l \) the light intensity at the center of the resolved spectral line absorbed in the atmosphere
- \( l_0 \) the light intensity at the same wavelength in the light source
- \( \sigma \) the absorption cross section of OH (\( \text{cm}^2 \)) at the particular wavelength for the rotational state being measured at finite resolution,
- \([OH]\) the number density of OH averaged over the light path (\( \text{cm}^{-3} \)),
- \( L \) the absorption pathlength (cm), and
- \( n/n_0 \) the fraction of OH molecules in the molecular level from which the absorption transition originates.

The cross section for each molecular rotational line is computed from

\[
(\sigma)_v = \pi r_0 f_v(1/\Delta \nu)(1/a),
\]

(4)

where \( f_v \) is the oscillator strength, \( r_0 \) the classical electron radius, \( \Delta \nu \) is the line width (\( \text{cm}^{-1} \)) (FWHM), and \( a \) is the Voigt shape factor. The actual cross section used for derivation of the OH concentration is computed using the spectral resolution of the spectrograph and the line broadening parameters for OH for the altitude, pressure, and temperature at Fritz Peak.

The light source chosen for this experiment is a commercial XeCl excimer laser (Questek, Inc. Model 2420) with modified optics (Mount 1992). This excimer laser has a spectroscopically broad output from the excited \((0, 1)\) and \((0, 2)\) XeCl vibrational bands, which covers a several tens of nanometer spectral window for each pulse. This window overlaps several of the OH rotational lines in the \( A-X(0, 0) \) system, thus allowing an independent determination of \([OH]\) from several OH lines simultaneously and giving a good spectral signature and an essential consistency check. The laser has a high photon output of approximately \( 10^{17} \) photons/pulse (100 mJ/pulse) and can be run at any repetition rate between 0.1 and 35 Hz. Laser beam divergence is measured to be \( 160 \ \mu\text{rad} \times 250 \ \mu\text{rad} \); this low value is essential to a strong return signal since the laser light travels over 20 km before detection. Figure 2 shows a single pulse spectrum of the laser output measured at spectral resolution approximately 200 \( \text{nm} \). The two broad peaks are the vibrational bands of XeCl.

It has proved to be absolutely essential to the determination of OH concentration to measure both the absorbed laser spectrum and the reference laser spectrum for each set of laser pulses in an integration due to the large (1–2%) spectral–spatial inhomogeneities in the
TABLE 1. TOHPE participants and measurements. Meteorological parameters were measured at both ends of the long path and at the Idaho Hill site; LP indicates measured on the 10.3-km long path by spectroscopic techniques; all others in situ.

<table>
<thead>
<tr>
<th>Measurements</th>
<th>Participants: Affiliation</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>F. Eische and D. Tanner: NCAR/Georgia Tech</td>
</tr>
<tr>
<td>OH</td>
<td>G. Mount: NOAA AL (LP)</td>
</tr>
<tr>
<td>OH</td>
<td>W. Brune and P. Stevens: Pennsylvania State University</td>
</tr>
<tr>
<td>OH</td>
<td>K. Mopper and X. Chen: Washington State University</td>
</tr>
<tr>
<td>HO₂</td>
<td>W. Brune and P. Stevens: Pennsylvania State University</td>
</tr>
<tr>
<td>HO₂ + RO₂</td>
<td>C. Cantrell: NCAR</td>
</tr>
<tr>
<td>j(O₃) and j(NO₂), biometer/Eppley cell</td>
<td>R. Shetter: NCAR</td>
</tr>
<tr>
<td>NO₂</td>
<td>E. Williams and K. Baumann: NOAA AL</td>
</tr>
<tr>
<td>NO</td>
<td>J. Harder: NOAA AL (LP)</td>
</tr>
<tr>
<td>NO</td>
<td>E. Williams and K. Baumann: NOAA AL</td>
</tr>
<tr>
<td>NO₅</td>
<td>E. Williams: NOAA AL</td>
</tr>
<tr>
<td>NO₅</td>
<td>S. Buhr and R. Norton: NOAA AL</td>
</tr>
<tr>
<td>NO₇</td>
<td>E. Williams and K. Baumann: NOAA AL</td>
</tr>
<tr>
<td>H₂O</td>
<td>J. Harder: NOAA AL (LP)</td>
</tr>
<tr>
<td>O₇</td>
<td>E. Williams and K. Baumann: NOAA AL</td>
</tr>
<tr>
<td>O₁</td>
<td>J. Harder: NOAA AL (LP)</td>
</tr>
<tr>
<td>CH₃O</td>
<td>A. Fried, S. Sewall, and B. Henry: NCAR</td>
</tr>
<tr>
<td>CH₄O</td>
<td>J. Harder: NOAA AL (LP)</td>
</tr>
<tr>
<td>SO₂</td>
<td>J. Harder: NOAA AL (LP)</td>
</tr>
<tr>
<td>Hydrocarbons (30 species)</td>
<td>P. Goldan and W. Kuster: NOAA AL</td>
</tr>
<tr>
<td>Aerosols: size and composition</td>
<td>D. Murphy and D. Thomson: NOAA AL</td>
</tr>
<tr>
<td>CO</td>
<td>J. Roberts: NOAA AL</td>
</tr>
<tr>
<td>CO</td>
<td>J. Brault and R. Jakoubek: NOAA AL (LP)</td>
</tr>
<tr>
<td>PAN</td>
<td>J. Roberts and S. Bertmann: NOAA AL</td>
</tr>
<tr>
<td>PPN</td>
<td>J. Roberts: NOAA AL</td>
</tr>
<tr>
<td>HNO₃</td>
<td>R. Norton and S. Buhr: NOAA AL</td>
</tr>
<tr>
<td>CH₄</td>
<td>J. Brault and R. Jakoubek: NOAA AL (LP)</td>
</tr>
</tbody>
</table>

**OH EXPERIMENT**

![Diagram](image)

Fig. 1. A detailed layout of the long-path OH instrument.
laser output (Fig. 3) and our inability to sample these in the two channels with the same spatial geometry since one beam remains in the laboratory (nominal near field) and the other travels many kilometers (far field). It has not been possible to either sequentially measure the laser spectrum within the laboratory and then measure an absorbed spectrum to determine the ratio in Eq. (4) or to perform any kind of curve fitting on the absorbed spectrum alone to fit the appropriate continuum and see absorption features at very small absorption levels. This requirement has appreciably complicated the experiment, although the ability to measure both channels was built into the design from the very start. It has especially complicated the design of the spectrograph (below) since optical illumination of the spectrograph optics must be the same in both channels and the spectral resolution of the two channels must be the same. The spatial sampling problems provide the basic limitation to sensitivity and precision at low OH concentrations to this experiment.

The mirror assembly that reflects the laser beam at 10.3 km from the observatory is a one square meter array of 121 small open retroreflectors. A retroreflector array was chosen over a steerable mirror system since 1) it returns light back on itself, thus eliminating any necessity for either initial or active alignment of the mirror system; 2) it allows the reflector unit to be used by several experiments simultaneously with minimal interference (there is some interference due to the diffraction lobes of the retroreflectors); 3) the return beam travels nearly the same path as the outgoing beam with a consequent reduction in scintillation; and 4) it converges coming back to its source, thus giving a signal increase instead of continuing to diverge as it would from a plane mirror.

In practice, the system requires retroreflectors with low divergence error (which depends on both accurate placement of the mirrors in each retroreflector and on accurate flat mirror surfaces) and high reflectivity. Measured divergence of the retroreflectors was $2 \pm 1$ arc seconds. Because the system must operate in the near ultraviolet, the retroreflectors purchased are of open construction with each surface magnesium fluoride overcoated aluminum. The size of the return beam at the observatory from the retroreflector array is approximately 75 cm in diameter. Divergence of the output laser beam has no effect on the size of the return beam (only on its intensity); rather the 75-cm beam size results from (at least) the optical imperfection of each retroreflector, the wavefront error on each face (which was measured with a red laser collimator system at several fringes), and the diffraction of the 6.2-cm diameter over 10.3 km. Since the return beam is centered on the source, the laser beam expander is located very close to coaxial with the receiver telescope at the observatory in order to maximize the return signal.

One of the major problems in using ultraviolet lasers to measure OH is that the laser beam generates OH in the atmosphere via Eqs. (1) and (2). In order to reduce this effect to a level below the detectability limit of the experiment, the 8-mm diameter laser beam is spatially expanded to reduce the flux density of the output. Flux density, rather than total photon output, is what determines the quantity of laser-generated OH. The beam is expanded using a small negative lens (AR coated for 308 nm on one side to eliminate any possible etaloning) to 15-cm diameter on a parabolic telescope mirror. The divergence of the laser beam along the path further decreases the beam flux density as does the scattering due to Rayleigh and Mie processes and ozone absorption. The (crudely) predicted amount of laser-generated OH is approximately 5000 cm$^{-3}$ averaged over the 20.6-km path. Measurements of concentration made at night,
when the expected natural background of OH is believed to be less than $10^4$ cm$^{-3}$, indicate OH levels that are below the sensitivity limit of this system ($5 \times 10^2$ cm$^{-3}$). Thus, laser-generated OH is not a perturbing factor in this experiment.

The telescope collector is a standard f/13 25-cm diameter Cassegrain system with magnesium fluoride overcoated aluminum mirrors. A dual channel 2-m focal length high-resolution echelle spectrograph has been designed and constructed specifically for this experiment. The OH rotational lines absorbed in the atmosphere at Fritz Peak are approximately 0.002 nm FWHM (Leonard 1990). Thus, a spectrograph with a resolving power of at least several hundred thousand is desired to resolve and sample individual rotational lines. It is very important to measure the OH rotational lines with high spectral resolution since maximum absorption depth is then measured with corresponding maximization of the signal to noise ratio. The spectrograph constructed for the OH experiment is a modified Czerny–Turner echelle design of speed f/20 and focal length 2 m. The grating is an old Bausch and Lomb 300 g mm$^{-1}$ echelle blazed at 63.5° and used in the 19th order to give a linear dispersion of about 0.034 nm mm$^{-1}$ in the focal plane. The grating was shifted off the optical centerline to meet the coma correction condition originally stated by Fastie (1961). The entire design was subjected to an extensive ray trace analysis. The program allowed interactive use of the computer in the design process, and all of the optical locations determined analytically were iterated using the computer to a position giving minimum image aberration in the spectrograph focal plane. Approximately 8% of the laser light is beam split by a wedged quartz window (4%/side, although only one reflection is used by the spectrograph) prior to the beam expander (see Fig. 1). The rest of the beam is transmitted to the retroreflector, absorbed in the atmosphere, and finally returned to the observatory. The reflected beam providing the reference spectrum $l_0$ is focused by a quartz lens onto a reflection diffuser in front of the entrance slit of the spectrograph. This reflection diffuser is carefully baffled from the other entrance slit, and extensive baffling inside the spectrograph prevents cross talk between the two beams. The amount of cross talk is easily measured by closing off the atmospheric entrance slit and measuring the signal in the atmospheric channel; the level is <0.1% of the atmospheric signal.

The detector used in the echelle spectrograph is a dual-Reticon silicon photodiode array system (type 1024 SAU-011) constructed at the NOAA Aeronomy Laboratory (Mount et al. 1992). This type of array detector was chosen for the following reasons: 1) It is a multiplexing system that requires no mechanical spectral scanning. 2) It has low readout and random noise properties, 3) for “large” photon levels it provides signal to noise ratios that cannot be matched by a photon counting device such as a photomultiplier system, 4) it is linear over a large dynamic range (tested to <0.1%), and 5) it is rugged and very suitable for field use. The chip is used without the commercially supplied protective quartz window to eliminate spectral etaloning from this element. The detector is used in a vacuum dewar containing the chip and associated preamplifiers. This dewar has a wedged (to prevent etaloning) quartz window on it for vacuum integrity. The detector is cooled to ~80°C by a five-stage Peltier cooler, and the dewar pressure of $2 \times 10^{-7}$ Torr is maintained by a vaccon pump. Pixel size is 25 μm (dispersion direction) × 2.5 mm. This pixel size is the ultimate limitation on realizable spectral resolution for the OH measurement. Spectra of the 546-nm Hg green line were used in determining the ultimate spectral resolution, which was measured to be 500 000 using a small 3-μm entrance slit and a microscope to observe the fine structure. Figure 4 shows a spectrum of OH in emission from a lamp, demonstrating the resolving power of the instrument with the array detector. Spectral resolution utilized for OH measurements was about 150 000. The detector exhibits noise of about three data numbers (2500 electrons) and a useful well depth of 2° data numbers (approximately 50 × $10^6$ electrons). This signal to noise level is essential to measurement of the small (few hundredths to few tenths of percent) absorption features from atmospheric OH.

A crucial test of the experiment is the ability to observe (in the $I/I_0$ ratio) artificially generated OH in the light beam directed to the retroreflector. A 15-cm long propane flame was placed in the return laser beam from the retroreflector array in front of the collector telescope at the observatory. OH is generated in copious amounts in the flame and should absorb light coming from the retroreflector at the wavelengths appropriate to the OH rotational lines. Figure 5 shows the raw observed ratio spectrum from the flame in the region of

![Intensities vs Wavelength](image-url)

**Fig. 4.** Spectrum of the region near the OH lines used for the determination of the OH concentration. The light, in emission, is from a low pressure Cu hollow cathode lamp used for wavelength calibration.
the OH lines. The OH lines are clearly visible at very high signal to noise ratio. This experiment clearly demonstrates the ability of the instrumentation to resolve OH absorption in the atmosphere. Figure 6 shows an example of OH absorbed in the atmosphere on the 20.6-km long path. Perturbations by other absorbers are clear. A paper on the 1993 long-path data is in preparation and includes detailed discussion of the analysis technique and examples of data at each stage of analysis.

3. Experiment description: White light

The determination of the concentrations of the molecules that affect OH abundance simultaneously with the measurement of OH is crucial to testing photochemical theories of OH formation and understanding the variations in the hydroxyl data. To this end, a second long-path experiment has been constructed to measure a number of tropospheric trace species. Figure 7 shows a schematic diagram of the instrumental arrangement. The light source is a 1000-W xenon arc. Figure 8 shows a spectrum of this lamp in the blue spectral region; note the large pressure-broadened Xe emission lines. These lines change in intensity with time. This lamp illuminates the focal point of a Newtonian telescope, which projects the beam 10.3 km across a valley to the site where the retroreflector array is located. The return beam is focused onto the entrance slit of a double-crossed spectrograph of 0.4-nm resolution after being collected by a 60-cm diameter parabolic mirror. The beam is guided onto the entrance slit of the spectrograph by an automated control system utilizing an interactive CCD camera that observes the image of the retroreflector on the mirrored spectrograph entrance slit and updates the position every 5 seconds. Guiding is required due to scintillation and building motion.

The second of the optical paths is used to monitor variations in the output of the arc lamp. The variation of the lamp spectrum with time, and our inability to monitor the spectral output simultaneously with the atmospheric measurements, is a major limitation on the experiment. This path employs two flat mirrors and two spherical mirrors to focus the arc onto a quartz diffuser plate that can be moved in front of the entrance slit.

The spectrograph is a 0.25-m focal length double-crossed Czerny–Turner design (to reduce scattered light). The spectrograph illuminates a diode array detector, as described above. Simultaneous spectral coverage is about 40 nm with 10 detector pixels on the full width at half maximum of a narrow spectral feature thereby oversampling the line shape.

Long-path spectroscopy provides a number of important advantages in measurement of tropospheric molecules. The technique utilizes the unique molecular spectrum of a molecule to identify its presence in the atmosphere. It allows simultaneous identification of several species and measures the concentrations without either physical or chemical transformation. A number of molecules have very distinctive spectra in the UV/visible spectral regions typically observed. Table 2 is a listing of the molecules currently under study and the wavelength regions where they are measured. Figure 9 shows the differential cross-sectional spectra of nitrogen dioxide taken with this instrument in the spectral region where it is most sensitively measured.

Figure 10 shows a raw spectrum of the atmosphere (plus lamp) in the blue spectral region. This spectrum was taken during a period of extreme pollution at Fritz Peak and shows very strong absorption from nitrogen dioxide (3.7 ppbv; clean air amounts are typically 60 pptv; our sensitivity limit is about 50 pptv at Fritz Peak).

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**FIG. 5.** The ratio of the absorbed beam from the retroreflector to the laser output with a 15-cm long propane flame placed in the light beam returning to the spectrograph. The flame generates copious amounts of OH, which are absorbed in the laser beam.

**FIG. 6.** The ratio of two spectra: one that has traveled 20.6 km to the retroreflector array and return and one that resided in the laboratory.
superposed on the lamp spectrum. Deduction of molecular concentrations proceeds from this measurement of the lamp spectrum absorbed over the long path. The physics is very similar to that of OH derivation given above and uses Beer's law in the form

$$I(\lambda)/I_0(\lambda) = \exp[-L\sigma_i(\lambda)c_i]$$

(5)

where

- $\lambda$ wavelength of light
- $I_0(\lambda)$ unattenuated intensity of the light source

Equation (5) is converted to a nonlinear matrix equation and solved using the method of singular value decomposition, minimizing in the least squares sense the residual absorption. The residual absorption is a measure of unknown molecular spectra in the atmosphere and various sources of noise (both random and systematic) that arise from the detector, inability to simultaneously measure the lamp spectrum with the atmospheric measurement, and inability to exactly remove the solar spectrum resulting from Rayleigh scattered light along the long path.

**Table 2. Sensitivity limits for the Fritz Peak long path white light experiment.**

<table>
<thead>
<tr>
<th>Species</th>
<th>Wavelength region (nm)</th>
<th>Sensitivity at STP (pptv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_2$</td>
<td>310–340</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>421–437</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>437–450</td>
<td>40</td>
</tr>
<tr>
<td>O$_3$</td>
<td>310–340</td>
<td>1000</td>
</tr>
<tr>
<td>CH$_3$O</td>
<td>310–340</td>
<td>120</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>310–350</td>
<td>60</td>
</tr>
<tr>
<td>NO$_3$</td>
<td>660–640</td>
<td>1</td>
</tr>
<tr>
<td>HONO</td>
<td>448–488</td>
<td>40</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>437–450</td>
<td>$2.5 \times 10^{14}$ molecules/cc</td>
</tr>
</tbody>
</table>

**Fig. 8.** The spectrum of the Xe arc in the blue spectral region.
Scattered sky light presents a special problem for this technique. It is necessary to preprocess this data to remove as much of this signal as possible prior to performing the nonlinear least squares analysis. The spectrograph entrance slit is carefully matched in size to the imaged size of the retroreflector in the telescope focal plane; thus, it acts as a mask to minimize the effect of spatially scattered light from the sun and from the light scattered from the ground near the retroreflector array. Scattered light from the sky and ground are determined in each measurement sequence by blocking the lamp beam to the retroreflector array, and this signal is subtracted from the signal determined in normal measurement mode from the retroreflector. This process removes most of the scattered light from the atmospheric measurement since the two measurements are not time coincident and, thus, may not be exactly comparable. The last step in the analysis procedure is to remove what remains of this solar signal in the nonlinear least squares procedure by fitting out the distinctive shape of the solar spectrum.

Figure 11 shows the raw spectrum measured in Fig. 10 with slope and curvature removed. The absorption by atmospheric species (mostly NO₂) is very apparent during this pollution episode of 3.7 ppbv NO₂. Figure 11 also shows this same raw spectrum superposed on an inverted differential cross-sectional spectrum of nitrogen dioxide. The correlation of most of the features is immediately apparent, indicating the presence of NO₂. Knowledge of the absorption cross section of NO₂ and the measured absorption of NO₂ in the troposphere on the 20.6-km path now allows a determination of the concentration of NO₂ at 3.7 ppbv. Similar pictures can be developed for ozone retrieval and other trace molecules in this and other spectral regions that particular molecular species absorb.

In practice, we solve for all molecular concentrations simultaneously in the nonlinear least squares. Concentrations are solved by the least squares procedure to
Fig. 12. Residual spectrum from 0916 LT 18 August 1993 during a period of moderate cloud cover and haze. The winds were westerly, and the NO$_2$ concentration was 804 pptv. The absorption spectrum prior to removal of NO$_2$ is shown as the dotted line. The residual absorption after the removal of NO$_2$ is shown as the solid line.

To minimize the residual spectrum. Residual absorption levels after removal of all we think we understand gives residuals of the order of 0.05%–0.15% peak to peak, depending on atmospheric visibility: this is then a measure of our lack of understanding of the atmosphere and of our noise sources. Figure 12 shows a typical residual in the blue spectral region.

An absolute differential absorption cross section for each molecule is measured on this spectograph. In this way, any possible distortions in the spectrum caused by the instrument function, or by grating anomalies, can be accounted for automatically. These effects are very difficult to remove from literature measurements of cross sections taken with different instruments at different resolutions. The spectra acquired on this instrument can then be compared against reliable literature values to obtain the absolute cross-sectional values. Further details of the measurement and analysis procedure are available in Harder and Mount (1991) and Harder et al. (1995). Figure 13 shows NO$_2$ data taken during the 1993 Tropospheric OH Photochemistry Experiment as a function of time, with data points every 6 minutes throughout this 24-hour period. Notice the large dynamic range of the NO$_2$ time series; thus, spectra must be acquired at least at this data rate in order to observe the effects of meteorological variability. Simultaneous data with long path measurements of OH is critical to the chemical interpretation.

4. The 1991 OH campaign—A summary

An informal OH intercomparison campaign took place in 1991 at Fritz Peak Observatory using the Aeronomy Laboratory OH instrument described above and the Georgia Tech instrument. Detailed results and interpretation have been described elsewhere (Mount and Eisele 1992; Eisele et al. 1994). Of the five-week period from 18 July to 24 August when the field study ended, only six days of good overlap data were taken. Many days were lost due to inclement weather since the summer was unusually cloudy and rainy. Some in situ and long-path ancillary measurements were performed including O$_3$ (long path and in situ), H$_2$O (in situ), NO (in situ), NO$_2$ (long path and in situ), NOy (in situ), CO (in situ), SO$_2$ (long path and in situ), CH$_3$O (long path), solar flux, temperature, and meteorological parameters.
The intercomparison of the OH data was complicated by the local in situ and long-path nature of the measurements. The long-path measurements integrate over a 10.3-km path that averages about 120 m above a forested valley. Thus, the long path may experience clean air flow along the entire path or some combination of clean and polluted air entering the path from the side canyons, which funnel air from the Denver metropolitan region during easterly airflow. Although clean air is normally experienced due to the westerly airflow, in the summer months the airflow often reverses in midday and becomes easterly. The in situ instruments measured locally at the end of the long path near the retroreflector array. On perfectly clear days, the solar flux, which directly affects the OH concentration, will be smoothly varying for both in situ and long-path instruments, and thus, the effect of solar flux on the OH concentrations is easily interpreted. However, during cloudy conditions the interpretation of the changes in solar flux along the long path were much more difficult. Percentage cloud cover along the path can be estimated from the video monitor of the long path, but quantification is difficult.

The relationships between NO$_x$, NO$_y$, and O$_3$ in this Front Range environment has been well established from a number of past field studies at Niwot Ridge (Parrish et al. 1986a; Parrish et al. 1990). Concentrations of NO$_2$ are highly variable in space and time and provide a sensitive indicator of the inherent differences between long path and in situ measurements. Relatively good agreement is seen between long path and in situ measurements of fairly stable species such as O$_3$. Long path and in situ measurements of shorter-lived species such as NO$_x$ differ significantly at times. In the absence of hydrocarbon measurements several discrepancies between long path and in situ measurements are presently unexplainable. The intercomparison of in situ and long-path data are analyzed in detail with the much more extensive dataset obtained during the 1993 OH campaign at Fritz Peak (Harder et al. 1995).

Figure 14 shows intercomparison data for a clean and clear day in August and demonstrates the generally good intercomparison found between derived OH concentrations between the two instruments. The hydroxyl radical concentrations near midday and under relatively clean air conditions quite consistently fall in the $2 - 3 \times 10^6$ cm$^{-3}$ range. These low values were lower than predicted by models (Eisele et al. 1994) based on inputs typical of the mountain area (Parrish et al. 1986a,b; Parrish et al. 1990) by large factors ($2 - 4$), and an unmeasured hydrocarbon scavenger was proposed as the removal mechanism. Approximately 2 ppbv equivalent isoprene was needed in the model to bring the OH concentrations down to the observed levels. While these concentrations may be considerably lower than model predictions, there is good similarity from one day to the next because the OH precursors (solar flux, H$_2$O, and O$_3$) were also fairly similar from day to day. A strong qualitative correlation of OH concentrations with NO concentrations and solar flux intensity was clearly observable.

The reader is referred to Eisele et al. (1994) for a detailed description of this campaign and the interpretation of the data.

5. The 1993 OH campaign

An extensive Tropospheric OH Photochemistry Experiment (TOHPE) was carried out in fall 1993 at Fritz Peak, Colorado. Table 2 lists the participants, their affiliations, and the species measured. The campaign took place from 16 August to 1 October and included intervals of summer and fall weather including clear and cloudy skies, and episodes of pollution and clean continental airflow.

Hydroxyl measurements confirmed the low hydroxyl values from the 1991 informal campaign during clean airflow (NO$_x < 200$ pptv) with peak concentrations near $3 \times 10^6$ cm$^{-3}$ at noon, thus indicating once again the presence of an OH scavenger in the boundary layer in this mainly pine forest region. Many interesting pollution episodes were measured including very rapid (minutes in both in situ and long-path measurements) changes in OH concentration in response to changes in other species and solar illumination. These episodes provide an extremely rigorous test of photochemical models with NO$_x$ ranging from 100 pptv to 8 ppbv on several days of extreme air pollution. Hydrocarbon measurements made before and after the snowstorm on 13 September indicated a significant decrease in local vegetative (natural) emission during clean westerly airflow, and this provided a good modeling opportunity for specific hydrocarbon effects on OH concentration.
Thousands of OH data points were taken during this campaign, thus providing an extensive dataset for not only intercomparison of hydroxyl under a variety of atmospheric conditions (e.g., clear/cloudy) but also a chance to evaluate OH concentrations under a variety of trace gas levels. The OH concentrations derived from the various experiments agreed within the error bars of the instruments (typically ±30%) most of the time; on the occasions when agreement was not good, the ancillary measurements almost always provided a mechanism for understanding the difference. For example, elevated NO on the long path (but not at Idaho Hill) could raise the OH concentration from the long-path instrument, but not from the in situ instrument. A number of episodes like this occurred.

The measurement of a number of different species not only provides an opportunity to understand the photochemistry of OH under varying conditions, but it also provides a unique opportunity to quantify in detail the problems associated with comparing in situ and long-path instrumentation. The results to date indicate a gratifying ability to predict the motion of air masses based on the response of trace species to air motion.

None of the results of the 1993 campaign are discussed here since, by mutual agreement among the experimenters, they are being discussed in detail in a special issue of the Journal of Geophysical Research.

6. Summary

We have discussed the long-path experiments, which measure OH and ancillary trace gas species at the NOAA Fritz Peak Observatory. These instruments utilize state of the art spectrographs and detectors to achieve very low sensitivity limits for measurement of a number of trace gases. The concentrations of trace species are determined using only simple physics and easily derived parameters, thus increasing their credibility. The techniques make use of several spectral absorption features, which improves confidence in the derived result. These instruments have recently been used in an extensive OH comparison campaign to deduce tropospheric OH concentrations to a sensitivity level of 5 × 10^5 cm⁻³ and measure ancillary trace gas species that affect hydroxyl concentration simultaneously.

Comparison of several methods of OH determination at two different campaigns have shown agreement within the overlapping error bars of the experiments. Hydroxyl concentrations measured are consistently low (3 × 10^6 cm⁻³) at noon during clean air conditions (NO₂ < 200 pptv) in a forested environment and rise under polluted conditions. This indicates the possible presence of an OH scavenger in the planetary boundary layer, which we do not at present understand.

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REFERENCES


—, and Collaborators, 1986b: Measurements of the NO$_2$–O$_3$ photo-
—, and Collaborators, 1990: Systematic variations in the concen-
tration of NO$_x$ (NO plus NO$_2$) at Niwot Ridge, Colorado. J.
Junkermann, J. Rudolph, B. Schubert, A. Volz, D. H. Ehhalt,
K. J. Rumpel, and G. Helas, 1987: Tropospheric OH concen-
trations: A comparison of field data with model predictions. J.
Atmos. Chem., 5, 185–203.
Platt, U., M. Rateike, W. Junkermann, J. Rudolph, and D. H. Ehhalt,
5159–5171.
Poppe, D., M. Wallasch, and J. Zimmermann, 1993: The dependence
of the concentration of OH on its precursors under moderately
—, and Collaborators, 1994: Comparison of measured OH concen-
Rodgers, M. O., J. D. Bradshaw, S. T. Sandholm, S. KeSheng, and
D. D. Davis, 1985: A 2-λ laser induced fluorescence field instru-
ment for ground based and airborne measurements of at-
of the OH concentration in ambient air. Geophys. Res. Lett., 14,
123–125.
Tanner, D. J., and F. L. Eisele, 1995: Present OH measurement limits
dissociation of ozone and resonance fluorescence of OH in am-
Weinstock, B., 1969: Carbon monoxide: Residence time in the at-