Monitoring potential photochemical interference in laser–induced fluorescence measurements of atmospheric OH

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Abstract. *In situ* laser-induced fluorescence measurements of atmospheric OH are susceptible to interference from laser generated OH, particularly in the troposphere. To quantify this interference we implement the addition of perfluoropropene, C_3F_6, for the chemical removal of OH from the ambient air. The removal rate of OH by C_3F_6 is determined in the laboratory using the discharge flow technique. Over the temperature range 249 to 296 K the rate constant is $(6.0 \pm 0.8) \times 10^{-13} \exp[(370 \pm 40)/T]$ cm^3 $molecule^{-1}$ s^{-1}, independent of pressure. *In situ* measurements using C_3F_6 addition are performed in both aircraft-borne and ground-based experiments. These studies show that laser excitation of the $^2\Sigma^+(v=1)\leftarrow^2\Pi(v=0)$ transition (282 nm) at high pulse repetition rates and low peak power can provide reliable and sensitive measurements of tropospheric OH.

Introduction

The OH radical is the principal gas-phase oxidant in the troposphere, determining the atmospheric lifetime and degradation products of many gases released into the atmosphere [*Crutzen*, 1973]. OH oxidizes gaseous sulfur species, for example $(CH_3)_2S$ and SO_2, enabling the formation of aerosols that serve as cloud nuclei. These mechanisms influence the global climate and control acid rain production. OH also initiates the formation of photochemical smog that produces ozone in polluted urban and upper tropospheric regions. In addition, the odd hydrogen family (HO_x = OH, HO_2, and H) plays a significant role in determining the loss rate of stratospheric ozone. Observations indicate that catalytic ozone losses by OH and HO_2 are prominent in the lower [*Wennberg et al.*, 1994a] and upper [*Jucks et al.*, 1996] stratosphere. The central role played by OH in regulating our atmosphere has prompted the development of precise methods for its quantitative detection [*Albritton et al.*, 1990]. Its minute abundance, reactive nature, and the potential interferences from other species have made this task challenging.

Among the current generation of instruments, those detecting OH by laser-induced fluorescence (LIF) in the ultraviolet (UV) promise high sensitivity and selectivity [*Crosley*, 1995]. A potential interference exists, however, in atmospheric OH measurements using this technique. The UV laser photon has enough energy to photodissociate O_3 present in the sampled air, producing $O(^1D)$. $O(^1D)$ can react with hydrogen containing molecules, principally H_2O and CH_4, generating OH. This chemistry is extremely fast: OH can be produced and detected during the same 10 nanosecond (ns) laser pulse. Since the generation of $O(^1D)$ and the subsequent detection of laser generated

OH is a two photon process, the production of $O(^1D)$ from O_3 photolysis is minimized by the use of low laser pulse energies. This design strategy was implemented in early balloon-borne LIF systems that used a high repetition rate, low peak power Cu vapor laser [*Stimpfle et al.*, 1988] to detect stratospheric OH without photochemical interferences. On the other hand, LIF instruments using high peak power, low repetition rate lasers for tropospheric OH measurements can exhibit significant contamination from laser generated OH [*Smith and Crosley*, 1990].

The most common methods for LIF measurement of OH use laser excitation of either the $^2\Sigma^+(v=0)\leftarrow^2\Pi(v=0)$ band at 308 nm or the $^2\Sigma^+(v=1)\leftarrow^2\Pi(v=0)$ band at 282 nm and detect the fluorescence of the excited OH at 308 nm. The $O(^1D)$ production from O_3 photolysis is two orders of magnitude lower at 308 nm than at 282 nm; thus the use of the 0-0 transition lowers the possibility of OH generation from $O(^1D)$ reactions. However, since the probe laser and fluorescence detection are both at 308 nm, the sensitivity of the 0-0 pumping technique is limited by the prompt scattering of the probe laser. Gating techniques can be used to minimize the laser scatter but these require low pressures (~5 torr) to extend the fluorescence lifetime beyond the laser pulse. The 1-0 band at 282 nm can be used at both high and low pressures because the laser scatter can be removed from the fluorescence signal at 308 nm by optical filtering. To minimize the potential photochemical interference, the Harvard HO_x instrument uses low pulse energies (< 2 µJ/pulse) at high repetition rates (6 kHz) to pump the 1-0 transition at 282 nm [*Wennberg et al.*, 1994b]. The velocity in the duct is kept sufficiently fast (> 30 m/s) to ensure that each laser pulse interrogates a fresh volume of air. Nevertheless, it is important to verify the absence of laser generated OH in the LIF instrument for a wide range of operating conditions.

In the design of the Harvard LIF HO_x instrument a method is implemented to directly monitor laser generated OH. A reactive scrubber, perfluoropropene (C_3F_6), can be added to the flow in sufficient quantities to remove ambient OH from the sampled air by reaction in a few milliseconds (ms). The amount of C_3F_6 added, however, is insufficient to affect the laser generated OH since it is created and detected in a single 10 ns laser pulse. Thus, OH measured with C_3F_6 added provides a means of quantifying the spurious signal.

The ideal OH Scrubber: C_3F_6

The scrubber is required to react fast enough with OH so that its addition in trace amounts will remove ambient OH in milliseconds. In the process it should not generate other radicals in order to avoid the complications of secondary chemistry. Additionally, it should not add to the hydrogen content of the air since rapid OH production by reaction with $O(^1D)$ can occur in the detection zone. This restriction excludes the use of hydrocarbons, which others have used to measure the laser gener-
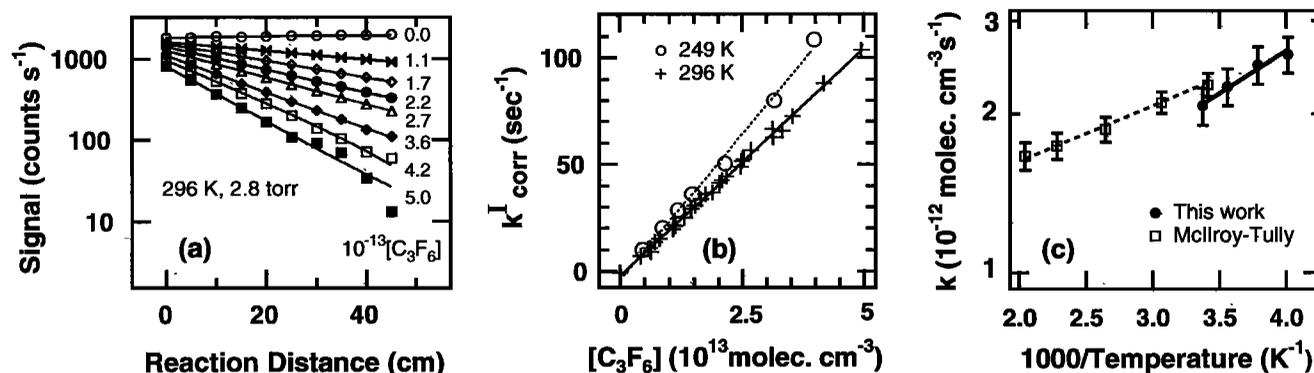
Figure 1. Kinetics of OH + C_3F_6 : (a) The OH fluorescence signal is plotted on a log scale against the reaction distance for experiments at 2.8 torr and 296 K. At right are the concentrations of C_3F_6. Distance is converted to time using the bulk flow velocity (v). The OH concentration is kept below 10^{11} molecules cm^{-3} to prevent OH regeneration. (b) The plot of the corrected decay rates $k^I_{corr} = k^I (1 + k^I D/v^2) + k^{probe}$, $\{k^I$ is the decay rate from (a), D is the OH diffusion coefficient in He, k^{probe} is the decay rate for $[C_3F_6] = 0\}$ against C_3F_6 concentrations, at 296 K and 249 K. The lines are weighted least squares fits whose slopes give the rate constants. (c) Rate constants are plotted on a log scale against 1000/Temperature for our results at 249-296 K and those of McIlroy and Tully at 293-489 K. The lines are the respective Arrhenius fits.

ated OH in tropospheric measurements [*e.g., Hard et al.*, 1992]. The scrubber should also have a negligible absorptivity in the vicinity of the laser wavelength, 282 nm. The temperature and pressure dependence of its reaction with OH should be weak. Its efficiency to quench the OH fluorescence should be small. It must be safe and commercially available in high purity.

S. P. Sander has suggested [*Smith and Crosley*, 1990] that the halogen substituted alkenes, which form strong adducts with OH [*e.g., Kirchner et al.*, 1990], would be suitable scrubbers for OH. The adduct produced in the reaction of OH with some chlorinated alkenes decomposes to produce Cl atoms [*Kirchner et al.*, 1990]. This makes the chlorinated alkenes unsuitable scrubbers for OH, since Cl reactions with ambient hydrocarbons can generate OH rapidly. We select perfluoroalkenes because the strongly bound fluorine substituents inhibit radical regeneration from the adduct. Perfluorination also suppresses the OH fluorescence quenching efficiency of hydrocarbons significantly. Furthermore, for the fluoroalkenes the UV absorption peaks around 160 nm, which is far enough from the 282 nm laser line to prevent interference from fluoroalkene photolysis. The use of tetrafluoroethene, C_2F_4, is impractical because it polymerizes explosively. Unlike the other haloalkenes, perfluoropropene is neither toxic nor inflammable, thus making it an ideal choice. Since C_3F_6 is a liquid with a modest vapor pressure (463–4896 torr) at atmospheric temperatures (232–298 K), it can be conveniently stored in a small lightweight bottle in the flight instrument. It is also readily available in high purity. We measured a negligible absorption cross section for C_3F_6 at 282 nm.

Discharge Flow Measurements of OH + C_3F_6

The successful implementation of C_3F_6 as a scrubber in the Harvard HO_x ER-2 instrument requires kinetic information on the OH + C_3F_6 reaction. In the absence of such measurements we estimate the rate constant to be in the range $1.5–3 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at room temperature from reactivity trends of other OH + haloalkene reactions [*Abbatt and Anderson*, 1991]. A slight negative activation energy (-0.7 to -1.0 kcal/mole) and negligible pressure dependence are anticipated. These kinetic predictions made C_3F_6 a plausible OH scrubber.

The rate constant and activation energy of the OH + C_3F_6 reaction is determined using the discharge flow technique [*Howard*, 1979]. Briefly, OH is generated by the rapid reaction of H with excess NO_2; $H + NO_2 \rightarrow OH + NO$. The H atoms are created by a microwave discharge of 2% H_2 in He. The OH radicals are added to a well developed laminar-flow gas stream of He in a teflon-coated glass tube (5 cm diameter). At the end of a reaction zone OH is detected by resonance fluorescence (sensitivity $\approx 10^{-8}$ counts s^{-1} $molecule^{-1}$ cm^3) at 308 nm using an OH lamp to excite the 0-0 vibrational band of the $A^2\Sigma-X^2\Pi$ electronic transition.

The reactant, C_3F_6, is added to the flow through a movable teflon-coated glass probe. All measurements are made under pseudo-first order conditions with the OH concentrations more than two orders of magnitude below C_3F_6 concentrations. The C_3F_6 (Matheson, 99.5%) is used as received; an FTIR spectrum is taken to check its purity. The only major impurities, as reported by the manufacturer, are C_2F_4 (< 0.5%) and air (< 0.5%).
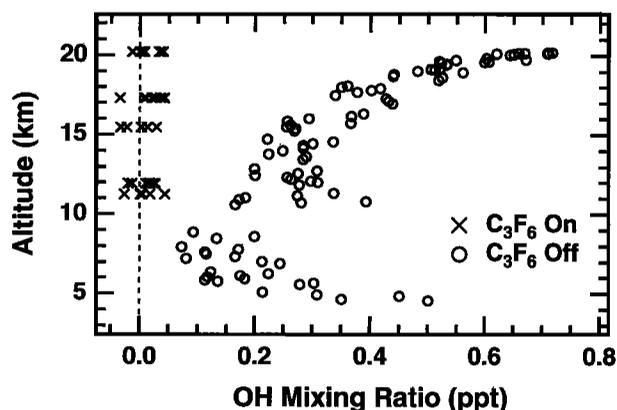
Figure 2. The OH mixing ratio measured on the ER-2 above NASA AMES on October 31, 1995 is shown versus altitude. The open circles are measurements with C_3F_6 off, corresponding to the ambient OH mixing ratio. The crosses represent the measurements with C_3F_6 on, corresponding to the signal with all ambient OH removed. The scatter in the crosses is approximately equal to the precision noise of the measurement.
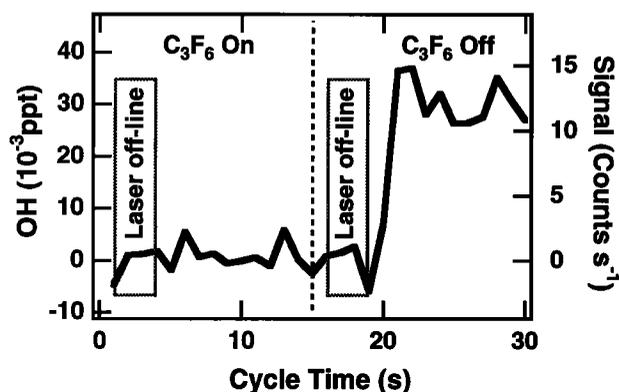
Figure 3. The OH signal measured from the second-story window of the Harvard Chemistry building between 10:00–11:00 AM on July 7, 1995 (SZA=35). The signal is an average of 37 measurement cycles, each lasting 30 seconds. Each cycle consists of 15 s with and 15 s without C_3F_6 addition. In each 15 s portion, laser scatter is measured with the laser off-resonance. Ambient OH is measured with the laser on-resonance and C_3F_6 off. The detected count rate (12 counts s^{-1}) corresponds to a mixing ratio of 0.03 ppt of OH in the flow tube.

Pseudo-first order decays are observed by fixing the C_3F_6 concentration and monitoring the drop in the OH fluorescence signal as the distance between the injection point and the detection axis is increased. The concentration of C_3F_6 in the flow tube is determined by measuring the rate of pressure drop in a glass reservoir of known volume. The reaction temperature is controlled by circulating cooled ethanol in the flow tube jacket. Pressure is measured at the center of the reaction zone and flowrates are measured by calibrated flowmeters. These are used to determine the bulk velocity from which we infer reaction time using the plug-flow approximation.

The experimental pseudo-first order decays are corrected for axial diffusion (<3%) and probe loss (<4 s^{-1}). A typical series of corrected OH decays for various C_3F_6 concentrations at 296 K and 2.8 torr is displayed in Figure 1a. The plot of the corrected decays against the C_3F_6 concentration is linear for all temperatures (*e.g.*, Figure 1b). At room temperature many such observations are made at several pressures ranging from 1.7 to 3.8 torr. A weighted least squares fit of these decays yields a bimolecular rate constant of $(2.1 \pm 0.2) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 296 K, independent of pressure. The error estimate includes known uncertainties. A weighted least squares analysis of the Arrhenius behavior of numerous measurements at four temperatures (29 at 296 K, 11 at 281 K, 9 at 264 K, 8 at 249 K) results in a temperature dependent rate constant of $(6.0 \pm 0.8) \times 10^{-13}$ exp[(370 $\pm$ 40)/T] cm^3 molecule^{-1} s^{-1}. The temperature dependent rate constants are shown in the Arrhenius plot in Figure 1c; the reported 2σ error limits include systematic errors.

A flash photolysis study of this reaction at higher temperatures (293–831 K) and pressures (75–750 torr) has been reported by *McIlroy and Tully* [1993]. Their rate constant measurement of $(2.26 \pm 0.12) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 75 torr and 293 K agrees with our low pressure observations. They also do not observe a pressure dependence in the 75 to 750 torr pressure range. Their conclusion that the high pressure limit is reached at a pressure below 75 torr is consistent with our observations. McIlroy and Tully report a highly structured Arrhenius plot with a negative activation energy below 489 K, and a positive activation energy above 656 K. This indicates a transition

in the mechanism from an addition reaction at low temperatures to an addition/elimination pathway at higher temperatures. They show that the HO-C_3F_6 adduct is stable with a long lifetime near room temperature. Their derived Arrhenius expression for data taken between 293–489 K, $(9.95 \pm 0.64) \times 10^{-13}$ exp[(245 $\pm$ 22)/T] cm^3 molecule^{-1} s^{-1}, is in good agreement with our result, considering that different techniques and temperature regimes are used (Figure 1c).

Chemical modulation of ambient OH

Stratosphere and Upper Troposphere: Extrapolating the measurements reported here to 230 K (lower stratospheric temperature), we estimate that for [C_3F_6] of 1–4 $\times 10^{14}$ molecules cm^{-3} the e-folding time for OH removal will be 3.2–0.8 ms. The reaction time available in the ER-2 HO_x instrument is typically 10 ms. This is long enough for OH to be removed from the ambient air before reaching the detection volume. However, the time scale for OH removal by C_3F_6 is considerably longer than the excitation laser pulse (10 ns) and has a negligible effect on the OH generated in the detection region. The mixing ratio of C_3F_6 used is too small to affect either the OH fluorescence yield or the $O(^1D)$ lifetime.

The ER-2 HO_x instrument detects the fluorescence signal from OH excited by a tunable laser via the $Q_1(2)$ transition of the $^2\Sigma^+(v=1)\leftarrow^2\Pi(v=0)$ band at 282 nm. OH signals are obtained with the laser tuned on-resonance with the $Q_1(2)$ transition, and background signals are measured with the laser tuned off-resonance. In the absence of laser generated OH, the addition of sufficient amounts of C_3F_6 will remove all ambient OH and reduce the fluorescence signal to background levels. If laser generated OH is present, the addition of C_3F_6 will reduce the fluorescence signal to some level above background. Calculations using the rate constant, the sampling duct cross-section, and the flow velocity in the instrument ensure that the addition of C_3F_6 (injected through a 70 sccm frit) at [C_3F_6] $\approx$ 2 $\times 10^{14}$ molecules cm^{-3} in the sampling duct, will reduce the ambient [OH] by 5 e-folds before the sampled air reaches the detection volume in the instrument.

This chemical modulation scheme was initially implemented in the Harvard HO_x ER-2 instrument during the SPADE (Stratospheric Photochemistry and Dynamics Expedition) campaign in the fall of 1992. *In situ* lower stratospheric experiments showed that OH LIF signals decay to background levels when C_3F_6 is added to the sampled air, demonstrating the absence of laser generated OH [*Wennberg et al.*, 1994b]. More recently, this technique has been implemented to verify the absence of laser generated OH in the upper troposphere. These measurements were made possible by the new flight profile of the ER-2, designed for obtaining upper tropospheric data. The flight included several constant altitude legs lasting 30 minutes each at altitudes between 11 and 20 km. *In situ* data shown in Figure 2 clearly demonstrate the absence of laser generated OH at altitudes above 10 km. These results are consistent with the absence of signal seen during nighttime (SZA > 110) when [OH] is expected to be very low.

Data below 10 km are not available for the C_3F_6 addition because the ER-2 did not perform cruise legs below this altitude. However, for the data shown in Figure 2, we estimate that the signal due to laser generated OH below 10 km amounts to less than 0.01 ppt. This is based on the analysis presented in *Shirinzadeh et al.* [1987] extrapolated to the conditions of our measurements (O_3 < 50 ppb; H_2O < 600 ppm; laser pulse energy

< 1 μJ; laser beam diameter ≈ 1.5 mm in the non-overlapping White cell). At higher O_3 concentrations or higher H_2O mixing ratios, however, we do expect significant interference, and thus addition of C_3F_6 will be useful to quantify the spurious signal.

Tropospheric Boundary Layer: The detection of OH by LIF in the lower troposphere and boundary layer requires careful investigation of laser generated OH because the mixing ratio of OH is low (< 0.1 ppt); thus, even small production of laser generated OH can result in significant error. The most promising ground-based technique for the measurement of OH with LIF is the expansion of ambient air through an orifice into a low pressure detection region [*e.g., Hard et al.,* 1992; *Stevens et al.,* 1994]. This technique has the advantage of decreasing the concentrations of species that contribute to the non-resonant fluorescence signal (SO_2, CH_2O) and of those that might contribute to laser generated OH (O_3, H_2O, hydrocarbons). In addition, the quenching rates of OH in the low-pressure sampling region are two orders of magnitude lower than at ambient pressures, thus the fluorescence quantum yield is accordingly higher. The disadvantage of this technique is the loss of OH on the orifice or on the walls of the low pressure region that has to be calibrated in the laboratory.

The interferences generated with the LIF technique in the boundary layer were examined by measuring OH from the second-story window of the Harvard Chemistry building. The air was sampled through an 0.23 cm diameter orifice mounted on the end of a 8 cm diameter, 100 cm long, halocarbon-wax coated flow tube attached to the duct of the HO_x instrument. Approximately 50 slm were pulled through the orifice using a large roots pump, resulting in a flow of 30 m/s at 3.5 torr. C_3F_6 was added to the flow through a 70 sccm frit ([C_3F_6] ≈ 10^{14} molecules cm^{-3}) at the end of the flow tube. By adding OH generated by a hot filament (> 1 ppt) to the flow we verified that this amount of C_3F_6 completely removed ambient OH before reaching the detection region. By adding a large amount of O_3 (>> 1 ppm) to the flow we confirmed that the added C_3F_6 did not affect the laser generated OH signal by more than a few percent.

Figure 3 shows the OH signal measured with C_3F_6 addition on and off. The signal with the C_3F_6 addition on is less than 1 count s^{-1} (≈ 0.003 ppt of OH). The lack of an observed interference is consistent with the analysis presented in *Shirinzadeh et al.* [1987]. Extrapolating to the conditions of this study (O_3 = 50 ppb; Relative Humidity = 55%; T = 304K; laser pulse energy ≈ 0.5 μJ; laser beam diameter ≈ 1.5 mm in the non-overlapping White cell), we expect to observe approximately 0.002 ppt of laser generated OH. The amount of laser generated OH is expected to increase linearly with both laser pulse energy, and the O_3 and H_2O mixing ratios. Under heavily polluted conditions or with significantly higher laser power, we would expect to see a significant interference; thus, C_3F_6 addition should be used to ensure an accurate ambient OH measurement.

The removal of OH by C_3F_6 is inappropriate when high concentrations of NO are present. For instance, HO_2 is measured by conversion to OH with the addition of NO. We see a large amount of OH upon adding C_3F_6 during our boundary layer HO_2 measurements. The presence of NO enables reactions that regenerate OH rapidly [*Donahue et al.,* 1996], thus disabling the C_3F_6 scrubbing mechanism.

Conclusions

Perfluoropropene is an ideal reagent to remove OH from sampled air to monitor any photolytic intereference in LIF

measurements of atmospheric OH. We measure rate constants for OH + C_3F_6 between 249–296 K to determine the amount of C_3F_6 required to completely remove ambient OH from the detection region of the Harvard ER-2 HO_x instrument. *In situ* experiments using C_3F_6 to chemically modulate OH in the ambient air demonstrate the lack of interference from laser generated OH in lower stratospheric and tropospheric OH measurements. We demonstrate that laser excitation of the $^2\Sigma^+(v=1)\leftarrow^2\Pi(v=0)$ transition using high pulse repetition rates and low peak power can be combined with chemical modulation to make reliable and sensitive OH measurements in the boundary layer.

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