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### Interference suppression in HO fluorescence detection

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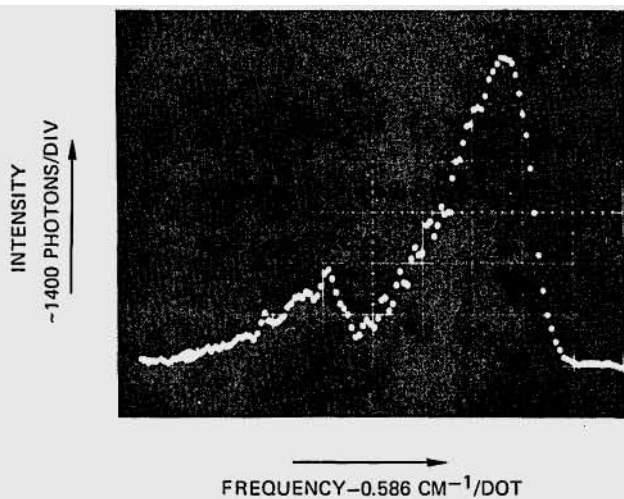


Fig. 1. CARS transmission through a 60- $\mu\text{m}$  diam, 20-m long optical fiber. The CARS spectrum was generated from  $\text{N}_2$  in a  $\text{CH}_4$ -air flame at 2100 K.

good, as seen in Fig. 1. There the CARS spectrum from the flame  $\text{N}_2$  is displayed with a spectral resolution of about  $1.9 \text{ cm}^{-1}$ , limited mainly by the vidicon cross talk. The spectrum was averaged on the optical analyzer for 10 sec, or 100 pulses. The photon level shown corresponds to a single shot average derived from the total count rate, number of pulses sampled, and vidicon quantum efficiency. The flame temperature determined by spectral fitting the contour of Fig. 1 was 2100 K and is described in more detail in Refs. 4 and 8.

That this approach is practically applicable has recently been demonstrated in experiments in an actual jet burner test stand. CARS temperature measurements from  $\text{N}_2$  were performed for two different liquid-fueled combustors, a swirl burner, and a JT-12 combustor can, situated in a 50-cm diam combustion tunnel. BOXCARS was employed to ensure good spatial precision. The aforementioned spectrometer and optical multichannel analyzer were situated in a control room adjacent to the burner test cell, and the CARS signals were piped out through rugged 20-m long, 60- $\mu\text{m}$  diam fiber optic cable (Siecior 133). Both average temperature measurements and single-pulse thermometry were performed. These experiments will be described in greater detail in a future publication.<sup>9</sup>

In summary, a new diagnostic advantage of CARS has been demonstrated, namely, the efficient, remote detection of CARS signatures using fiber optic guides. Such an approach will be highly useful in CARS applications in instrumentally hostile environments.

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## Interference suppression in HO fluorescence detection

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The free radical hydroxyl (HO) is of central importance in atmospheric chemical processes. Measurements of its concentration in ambient air are often performed with the sensitive technique of laser-excited fluorescence,<sup>1-3</sup> but many difficulties are encountered. These difficulties arise from the high reactivity of HO (and its consequent low concentration and short chemical lifetime), its low fluorescence yield at atmospheric pressure, and interferences near the detection wavelength (309 nm) by other substances in air. These interferences include (a) Rayleigh and particulate scattering at the excitation wavelength (282 nm); (b) Raman scattering by  $\text{O}_2$  (295 nm),  $\text{N}_2$  (302.5 nm), and  $\text{H}_2\text{O}$  (315 nm); and (c) fluorescence throughout this spectral region by unidentified air constituents.<sup>1,2,4</sup> These interferences are most severe at low atmospheric altitudes. They are attenuated by spectral filtering, and what remains of them is measured by the background obtained by off-resonance excitation. Provided that photochemical production of spurious HO is absent, the noise associated with this background determines the lowest HO concentrations that can be measured.

In this Letter we report preliminary results on a sampling method that greatly reduces the above interferences relative to hydroxyl fluorescence. The method involves expansion of the sampled air from 1 atm to lower pressures and takes advantage of the fact that the HO fluorescence yield is inversely proportional to the total pressure. Rayleigh, particulate, and Raman scattering decrease linearly with the pressure. Furthermore, it can be shown<sup>5</sup> that background fluorescence decreases from those air constituents whose fluorescence yield is higher than that of HO.

The present results were obtained in laboratory air, into which HO concentrations near  $10^{10} \text{ cm}^{-3}$  were introduced from a flowing source. The source produced HO by 185-nm photolysis of  $\text{H}_2\text{O}$  in  $\text{N}_2$  by a mercury lamp. The air mixture was continuously sampled by an 0.7-mm i.d. orifice leading into the side of a 10-mm i.d. Suprasil flow tube. Allowing the  $\text{N}_2$  flow to bypass the  $\text{H}_2\text{O}$  bubbler extinguished the HO signal. The flow-tube pressure was adjusted over the range 18-600 Torr by a valve leading to a vacuum pump.

Traveling along the axis of the flow tube was a beam of 8-nsec pulses of 282-nm radiation obtained from a frequency-doubled Rh-6G dye laser pumped by a frequency-doubled Nd:YAG laser. For these experiments the 282-nm pulses had an energy of 0.1 mJ and a spectral full width at half-maximum (FWHM) of  $1.3 \text{ cm}^{-1}$ . Fluorescence from a 2-cm length of the beam was collected, filtered by cellulose triacetate film and a 2.8-nm bandpass 0.25-m monochromator, and detected by a photomultiplier.

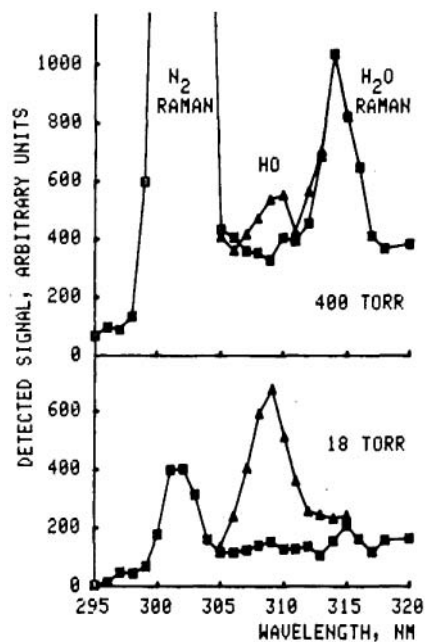


Fig. 1 Emission spectra obtained from 282-nm excitation of laboratory air mixed with a flowing HO source and sampled by an orifice, at flow-tube pressures of 400 Torr and 18 Torr.  $\Delta$ ,  $Q_{11}$  excitation.  $\blacksquare$ , nonresonant excitation.

The  $E$ -vector of the excitation beam was normal to the plane of observation, and no polarizer (other than the monochromator grating) was inserted into the detection path. This arrangement was chosen to maximize the strongly polarized Rayleigh and Raman interferences relative to the unpolarized HO fluorescence and to provide a rough intensity calibration.

Despite the high surface reactivity of HO we have observed useful chemical transmission of HO by the orifice and flow tube. Spectra obtained at flow-tube pressures of 400 Torr and 18 Torr are compared in Fig. 1 on the same ordinate scale. The HO signal is the difference between the fluorescence excited at  $Q_{11}$  (281.9145 nm) and that excited at a wavelength 0.024 nm longer. First, one notes the expected decrease in  $N_2$  and  $H_2O$  Raman intensities in going from 400 Torr to 18 Torr. Second, the fluorescent background at 309 nm improves, though not in proportion to the pressure change. Third, the HO signal grows with decreasing pressure, for reasons currently unclear. Expansive cooling increases the fractional occupancy of the HO rotational level that is being pumped at  $Q_{11}$ , but, at the flow velocities attained, the cooling is insufficient to account for the increase. We are inclined to attribute the observed growth in HO signal to decreasing wall loss in a turbulent zone immediately after the orifice.

With the HO source removed, the flow-tube pressure dependence of the room-air background fluorescence at 309 nm was measured (Fig. 2). Theoretical curves are included for the expected fluorescence signal, relative to 1 atm, for the case of HO and for two hypothetical substances whose fluorescence yields at 1 atm are 0.075 and 0.5. Evidently most of the observed fluorescence is due to substances whose yields are much higher than that of HO.

These experiments demonstrate the suppression of interferences and the preservation of hydroxyl fluorescence when air is expanded. Work toward improving the chemical transmission of HO by the orifice and flow tube is in progress.

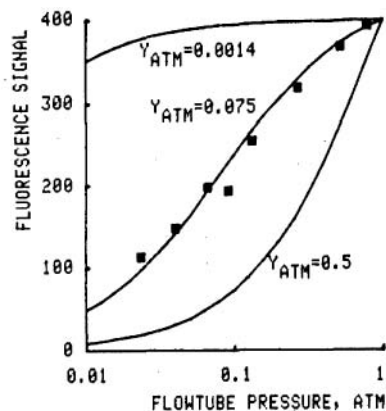


Fig. 2 Fluorescence of laboratory air excited at 282 nm and observed at 309 nm vs flow-tube pressure, compared with fluorescence behavior expected for HO (1-atm fluorescence yield  $Y_{atm} = 0.0014$ ) and for substances with  $Y_{atm} = 0.075$  and 0.5.

The HO fluorescence decay time, which is indistinguishable from the laser pulse width at 1 atm, lengthens with decreasing pressure, so temporal discrimination against interferences is also being investigated. Improvements in excitation power and linewidth and in signal collection and detection are anticipated; they will enable us to extend these studies to ambient HO in outdoor air.

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## Optical polisher for toroidal mirrors

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Toroidal mirrors are optically superior to spherical mirrors in applications, for example, as focusing and collimating mirrors for VUV and x-ray spectrographs or laser cavity resonator mirrors. Toroids are quite difficult to fabricate by conventional optical techniques, and, although a machine for making toroids is available commercially,<sup>1</sup> it is expensive, and its use is limited to two-axis optics. It would be desirable to have an adapter that could be added to an existing polishing machine to enable toroids to be polished and at the same time not interfere with the use of the machine as a conventional optical polisher for flats and spherical surfaces. Additional requirements of a toroidal polisher are that (1) the motion produced by the polisher be along two axes at 90° to each