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TWO-PHOTON LASER-INDUCED FLUORESCENCE DETECTION OF OH

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The TP-LIF OH sensor is based on the principle that a molecule having multiple energy states, all of which are bonding, can be pumped into the highest state with the resulting fluorescence being blue-shifted relative to all pumping wavelengths. In this way, one can successfully discriminate against virtually all noise sources in the system using long wavelength blocking filters in conjunction with solar-blind photomultiplier tubes. Thus, these systems tend to be "signal limited" rather than "signal-to-noise limited" as is true of the SP-LIF technique as well as other conventional analytical methods. The trick to achieving the above sampling scheme, with high efficiency, is in the use of high photon fluxes of short time duration. Obviously, the latter type of light source is fulfilled nicely by available pulsed lasers. From an operational point of view, however, this laser source needs to be tunable. The latter characteristic permits extremely high selectivity for the detection of a diatomic or simple polyatomic molecule by taking advantage of the high-resolution spectroscopic features of these type species.

The Georgia Tech group has now applied this multi-photon LIF detection scheme to several chemical systems including: NO, Hg, I_2, and OH. The most extensively developed system is that involving the detection of NO. This TP-LIF system has undergone both extensive ground-based and airborne field testing.

The current TP-LIF OH system exists in prototype form only; even so, it has enabled us to carry out proof-of-concept tests and in addition has permitted a realistic appraisal of two of the major questions related to the LIF detection of OH: (1) UV laser generated OH interference; and (2) non-resonance fluorescence background noise.

The prototype TP-LIF OH system is based on the sequential pumping of OH from $^2\Pi$, v"=0 to $^2\Pi$, v"=1 or 2 followed by electronic pumping of the $^2\Pi$ (v"=1 or 2) state to $^2\Sigma$(v'=0 or 1). The shortest pumping wavelength required in either of these schemes is ~ 347 nm whereas fluorescence occurs at ~ 309 nm. Based on the results derived from the prototype system, projected detection limits for OH under tropospheric conditions range from the low 10^4 to the low 10^5 molecules/cm^3 for a 10-minute integration time. The major requirement in moving the existing prototype system to the above stated level of performance is the availability of a high-energy IR pulsed laser centered at ~ 1.4 or 2.8μm. A discussion of possible future IR laser sources which will meet our requirements as well as other operational characteristics of the TP-LIF OH system will be presented during the H_xO_y workshop.

Comments

The two-photon method of detection of OH has been demonstrated only in a laboratory instrument although, these investigators stress, two-photon detection hardware for NO has proved flight worthy. This was thought of by most of the participants as a valuable third technique, behind the long-path absorption and reduced pressure methods, which would be ready in 2 or 3 years.

A major question raised was the ease with which the required pulse energy (200 mJ per pulse) in the infrared could be generated. There are several possibilities, all yet to be evaluated: (i) A titanium-sapphire tunable laser, Stokes-shifted twice in H_2; this will require 1 to 1.5 years development; (ii) An efficient infrared dye pumped by Nd:YAG 1.064 μm radiation, which has been demonstrated in Japan and the dye delivered to Georgia Institute of Technology; within a year it should be known how well this can be operated; and (iii) An I_2 laser which, when Stokes-shifted once, may have a coincidental overlap with an OH line; borrowed from the manufacturer, this possibility can be checked within the year.

Interference levels are quite low using this method. At 60 ppb, the O_3-H_2O laser-created OH will cause background signals equivalent to <5000 OH per cm^3. Photolysis of HNO_3 at 100 ppt yields OH signals of 70/cm^3, and that of H_2O_2 at 1 ppb gives an OH signal of 10/cm^3. This group estimates an overall calibration accuracy of 20 percent, deduced from an examination of the methods (H_2O_2 and O_3-H_2O photolysis) in the CITE-I evaluation. With 1 to 10 minutes averaging time, an overall accuracy within a factor of 1.5 is expected, with detectable limits lower than 10^5/cm^3 at a signal-to-noise level of unity.