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p. 2

OH MEASUREMENT BY LASER LIGHT ABSORPTION

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Since the first attempt to measure atmospheric hydroxyl radicals by optical absorption in 1975 (Perner et al., 1976) this method has been continuously developed further and its major obstacles and limitations are known today (Huebler et al., 1984). Three groups in Germany at Juelich, Frankfurt and Goettingen use the long-path absorption method and a fourth experiment is being built at the Max-Planck Institut in Mainz and a number of points have to be considered.

1 The laser beam needs to be expanded in order to reduce the beam divergence. At the same time the energy density of the laser beam which produces OH via ozone photolysis is reduced to such an extent that the self-produced OH concentration ranges well below the atmospheric value.
2 Atmospheric absorptions should be observed over a wide spectral range (40 cm^{-1}) so that not only the OH radicals are properly identified by several rotational lines but their absorption can be corrected for interfering absorptions from other air constituents as SO_2, CH_2O, CS_2, etc. which can be identified in a wide spectral range with more confidence.
3 Air turbulence demands fast (within about 100 µs) spectral scanning or probing on and off the absorption line.
4 Energy requirements should be kept small in field operations.

In the experiment frequency doubled dye laser pulses at 308 nm are produced. The picosecond light pulses are expected to show a smooth profile (light intensity against wavelength) which will be broadened to the required spectral width according to the uncertainty principle. The pump laser will be an optoacoustically modulated Nd:YAG laser.

After its path through the atmosphere the light is dispersed by a spectrograph of 0.1 cm^{-1} resolution and simultaneously collected by the 1024 channels of a photodiode array. According to a calculation based on the level of light seen by the detector a sensitivity of 105 molecules OH cm^{-3} along a 10-km path is expected for 2 minutes integration time.

Perner, D., D.H. Ehhalt, H.W. Paetz, U. Platt, E.P. Roeth and A. Volz, OH-radicals in the lower troposphere, Geophys. Res. Lett., 3, 466-468, 1976.

Huebler, G., D. Perner, U. Platt, A. Toenissen, and D. Ehhalt, Groundlevel OH radical concentration: New measurements by optical absorption, J. Geophys. Res., 89, 1309-1319, 1984.

Comments

These two variants on long-path absorption, to be developed at Mainz and Jülich, were both presented by Platt; the comments were directed at long-path absorption in general.

Platt estimated that contributions to the accuracy were 10 percent from systematic errors and 25 percent from the signal-to-noise ratio. It was felt that this method should be moved out of Jülich as soon as possible and into an environment which is neither dirty nor a desert (that is, where one can gain some understanding of the [OH] in a clean region which does contain the radical). The long-path absorption was viewed by most of the workshop participants as a primary check, not subject to serious systematic errors. Not discussed at the workshop, however, were the concerns about averaging [OH] and the other controlling variables and their influence upon comparison with models and other measurement results.

The $Q_1 1$ line is used for the measurement because it is the strongest; the interferences due to CH_2O and SO_2 are about the same for all strong lines. Some of the panelists felt that an effort should be made to consider determining a correlation among multiple peaks to avoid the interferences.

The rapid-scan method at Jülich is designed to avoid atmospheric turbulence; noise (variations in the spectral/temporal mode patterns) in the laser has not been considered. Also at Jülich, a low-pressure sampling cell measurement of [OH] is beginning. This is similar to the Portland State technique, although 308 nm excitation will be employed and gain-switching time-gating will be used.