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Optical Measurement of SO_2 in Combustion Environments

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Sulfur dioxide has been measured in a high temperature combustion environment by ultraviolet absorption spectroscopy and by Tunable Atomic Line Molecular Spectroscopy (TALMS). Measurements are made in the post-flame region of a flat flame burner using stoichiometric and lean methane/air mixtures doped with SO_2.

TALMS is an _in situ_, line of sight technique that uses a Zeeman-tuned atomic emission lamp as the light source. In these experiments the Zn line at 213.8 nm ($^1S_0 \rightarrow {}^1P_1$ transition) is used with the light parallel to the magnetic field. Detection of SO_2 is accomplished by magnetically tuning one of the Zeeman components into resonance with a specific absorption in SO_2 while using the other component as the reference signal. The two components are very close in frequency (~20 GHz), but differ in polarization, with the $\Delta M = +1$ transition right circularly polarized, and the $\Delta M = -1$ transition left circularly polarized. The differences in frequency and polarization form the basis for molecular detection with TALMS. A variable phase retardation plate then converts these beams into two perpendicular linear polarized beams, which are subsequently separated by a linear polarizer prior to detection by a photomultiplier tube. Both beams traverse an identical optical path, thus permitting good correction of the signal in highly scattering or absorbing systems, such as those encountered in sooting flames. The high selectivity of the technique greatly reduces interference by other molecules that absorb in the same spectral region.

Because of the complexity of the ultraviolet absorption spectrum of SO_2 in the 200.0 to 220.0 nm region it is not possible to identify the particular transition that causes the TALMS signal. The dependence of signal strength on magnetic field obtained at 1500K is equivalent to that determined at 300K, confirming that the same transition is measured in the flame system as under ambient conditions. The maximum TALMS signal occurs at a magnetic field strength of 14.5 kgauss.

The sensitivity of the TALMS technique varies with the temperature of the sample. For a 7cm path length at 1 atmosphere, the mininum detectable concentration is 40ppm at 300K, and 2000ppm at 1500K. Density differences due to combustion account for a factor of 5, and broadening of the absorption features at the higher temperatures reduces the sensitivity by an additional order of magnitude. The ultraviolet absorption spectrum of SO_2, measured as a function of temperature in the 300 to 1500K range, indicates the discrete absorption features gradually broaden as the temperature increases, and the underlying continuum becomes even more absorbing. This broadening is largely due to redistribution of the rotational level populations at the elevated temperatures, with the result that fewer molecules are in the particular state probed by the Zn line.

The TALMS signal is linear with SO_2 concentrations below 20,000ppm, while the absorbance at aproximately the same wavelength is linear at concentrations as high as 30,000ppm. This indicates that the fall-off in the TALMS signal is not attributable to self absorption or deviations from Beer's law, but is inherent to the TALMS technique. The non-linear region can be avoided by the proper choice of path length.

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