Two-Laser Differential Absorption for Wide Molecular Bands

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ABSTRACT

To measure trace concentrations of the atmospheric radical NO_3 we are investigating the use of two amplitude stabilized diode lasers, one tuned to the center of the absorption profile, and the second tuned to a wavelength outside the absorption. This approach is taken because the absorption feature is much broader than the visible diode laser's tuning range and removing the sample concentration from the beam path to measure the baseline is difficult. This paper describes the preliminary system design, interferences expected from water, and electronics design.

Keywords: NO_3, differential absorption, atmospheric monitoring, amplitude stabilization

2. INTRODUCTION

We report here on the preliminary design of a two-laser absorption spectrometer to measure atmospheric concentrations of NO_3. The absorption at two wavelengths, separated by approximately 10 nm will be measured differentially, instead of using one wavelength to probe the sample. Sensitive absorption measurements are usually accomplished with one laser by modulating the signal in some fashion, usually either by wavelength modulation or by periodically switching the beam path between a reference and the sample. To actually quantify the absorption measurement requires that the laser be tuned completely off of the absorption profile or alternatively that the sample be removed from the beam path to obtain a "zero absorption" baseline signal. The measurement of NO_3 in the atmosphere by visible diode lasers precludes these usual approaches because the absorption profile is much broader than the laser's tuning range, and it is difficult to remove the sample concentration from the beam over a long open-air path.

NO_3 is an atmospheric radical thought to play a significant role in the oxidation of various trace species at night.[1] In remote regions, the atmospheric concentrations of NO_3 are a few parts per trillion (10^{-12}), while in urban areas the concentrations can be significantly higher, since NO_3 is a product of NO_x chemistry. The goal of this instrument design is a noise equivalent detection of 1 part per trillion (1ppt), or 2.5×10^7 molecules·cm^{-3}. As discussed below, this will require at least a 100 m path length through air to achieve this sensitivity.

To determine the zero absorption baseline, the NO_3 concentration in an absorption cell may be reduced or eliminated by several means, including back-filling with a known gas, chemical titration with NO, or possibly by photolysis using short wavelength lamps. Over an open-air path none of these options are practical. Although in the initial phase of this work we are planning to use a multipass absorption cell, an approach applicable to long path measurements in air is desired since the measurement of even smaller concentrations of NO_3 (< 1 ppt) may well require extending the path length beyond 100 meters. Furthermore, a measurement technique which minimizes the time spent on determining the baseline signal in the multipass cell is of interest because this may increase the measurement time and reduce the time spent on gas handling.

At atmospheric pressure the NO_3 spectrum (Fig. 1) shows strong unresolved absorption in the red near 662 nm, with a full-width at half maximum of approximately 3 nm.[2] At the peak absorption, 1 ppt concentration corresponds to an absorption of only 5×10^{-6} over 100 m. The primary infrared absorption band (near 13.1 μm) is much weaker than the visible 662 nm band. Inexpensive diode lasers with moderate (5 mW) powers are available at the red wavelength, and with the proper temperature and injection current adjustments a given laser will often operate nominally in a single mode at a wavelength near the peak NO_3 absorption, with side-modes that are down by at least 13 dB. However, these solitary chip lasers can not be tuned off of the absorption profile by current or temperature without inducing large changes in the mode structure.
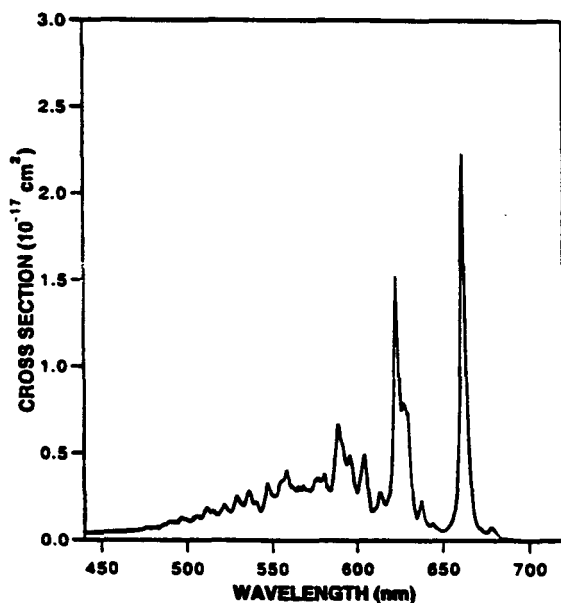

Figure 1. NO_3 visible absorption spectrum at 298 K. The peak at 662 nm is the O–O band, with a width of about 3 nm FWHM. The data plot is from reference 2.

Building a laser into an extended cavity configuration (ECL) would allow tuning over the necessary wavelength range. However, this is a much more expensive, more complex, and less robust solution than using solitary diode lasers.

The differential absorption approach taken in this work uses one laser tuned to a wavelength near or at the peak NO_3 absorption, and the second tuned to a wavelength near 671 nm. Care is taken that neither laser is tuned to an H_2O absorption. If the two beams traverse some atmospheric path length collinearly, and then are detected individually, the ratio between the detected signals is an estimate of the differential loss between the two beams. If NO_3 is the only absorber present in detectable quantities, this ratio is a measure of the exponential loss (I/I_0) of the 662 nm beam. This approach affords some common-mode rejection to the extent that perturbations affect both beams equally. For instance, degradation of the multipass cell mirrors' reflectance due to atmospheric contaminants would affect both laser beams, and at least to first order would not present a signal drift. Similarly, acoustic noise coupled into the absorption signals by dust on the optics may be less of a problem than in the case of a one laser system. Vibrational noise due to optical etalons is not cancelled out by using the two wavelengths, but may be reduced by shifting the fluctuations to higher frequencies, followed by averaging.[3]

Atmospheric water has a number of weak absorption lines within the NO_3 absorption peak at 662 nm. The expected water absorption profile was calculated using data from the Hitran96 database.[4] The strongest line results in an absorption of as much as 3×10^{-3}, for a 100 m path length and 40% humidity. However, near the maximum of the NO_3 spectrum there are a number of narrow bands (approximately 0.05 nm wide) in which the calculated absorption due to water is only a few parts in 10^{-6}. Absorption due to NO_3 can be monitored by tuning the laser wavelength to one of these narrow bands, and also monitoring the humidity of the air drawn into the multipass cell. This will allow us to make a small correction to the 662 absorption to compensate for the water absorption.

Another option is to tune the laser wavelength to 660.9 nm, where the water absorption is approximately 5 times less; although the NO_3 cross-section is down to 68% of it's peak, this would

eliminate the need for a humidity sensor and the data correction. At 671 nm the corresponding absorption due to water is negligible.

3. SYSTEM DESIGN

A system limited by the shot noise of the detected photocurrents is a useful point of comparison. The factors which may increase the minimum detectable concentration from the shot-noise-limited case include the lasers' amplitude noise, electronics noise, and etalons due to the optical elements. Furthermore any perturbations which affect the two beams differentially (such as vignetting or birefringence) must be avoided. The accuracy is determined primarily by the presence of trace amounts of other absorbing species at the two laser wavelengths. The Hitran96 database, which includes transitions from approximately 35 molecules, lists only water transitions in this wavelength region.

To avoid differential perturbations, the beams are overlapped to the greatest extent possible by spatially filtering using a single-mode optical fiber. The two collinear lasers' powers can be separately monitored by a number of different methods, for instance by amplitude modulation at different Fourier frequencies. Diffraction gratings are used in our present setup (see Fig. 2). The beams are split apart dispersively after the beamsplitter for intensity stabilization of each laser and again after the absorption cell for signal detection. Gratings with a frequency of 2400 lines·mm^{-1} are used at an angle of incidence of 45°, which results in an angle of separation between the two wavelengths of about 3°.

3.1 Intensity Control

Each laser beam is sampled by a beamsplitter ahead of the absorption cell, and a feedback loop to the injection currents is employed to reduce the intensity fluctuations. Approximately 40% of each laser's power is transmitted through the beamsplitter and is used for the control loops. With sufficient loop gain, the power fluctuations on the reflected beams can be reduced to about 4 dB above the fundamental shot noise limit. The servo loop bandwidths are about 1 MHz, and the loop gain curves are tailored to provide ≈100 dB of gain at 1 kHz. The offset currents which are summed with the photocurrents to generate error signals are derived from the same well-filtered voltage reference with 10^{-6} /°C stability. Often, the primary sources of noise in AM control loops are that the beamsplitter R/T ratio is not stable (for instance because of changes in the incident polarization) or that the photocurrent in the control loop is not a true representation of the reflected beam's power fluctuations. As an example, multiple reflections between the silicon photodiode surface and the glass detector package can transfer acoustic vibration noise to the photocurrent signal (for this reason the glass covers of all the detectors are removed). A thick (~7 mm) dielectric coated beamsplitter is used to prevent the second surface reflection from overlapping the first surface reflection. In addition, inadvertent optical feedback to the laser diodes will increase the intensity noise and is avoided here by the use of an angle-polished fiber and a 38 dB optical isolator.

3.2 Signal Detection

After the multipass cell, the two wavelengths are separated and individually detected. The photocurrent fluctuations are still limited by optical etalon effects as discussed below; however, in the absence of this noise (with the cell removed) and with 300 μA of photocurrent, voltage noise density at the transimpedance amplifier outputs is on the order of 1 μV/√Hz over the frequency range of 0.1 Hz to 50 kHz. The 300 μA of photocurrent is converted to a dc signal of 10 V. The amplifiers are bandwidth limited with a single RC roll-off at 10 Hz. Very low offset voltage, dual matched operational amplifiers are used to minimize the output voltage drift due to the electronics. The difference between the offset voltage drifts of the two amplifiers is specified as less than 0.3 μV/°C, which is less than 10^{-6} of the 10
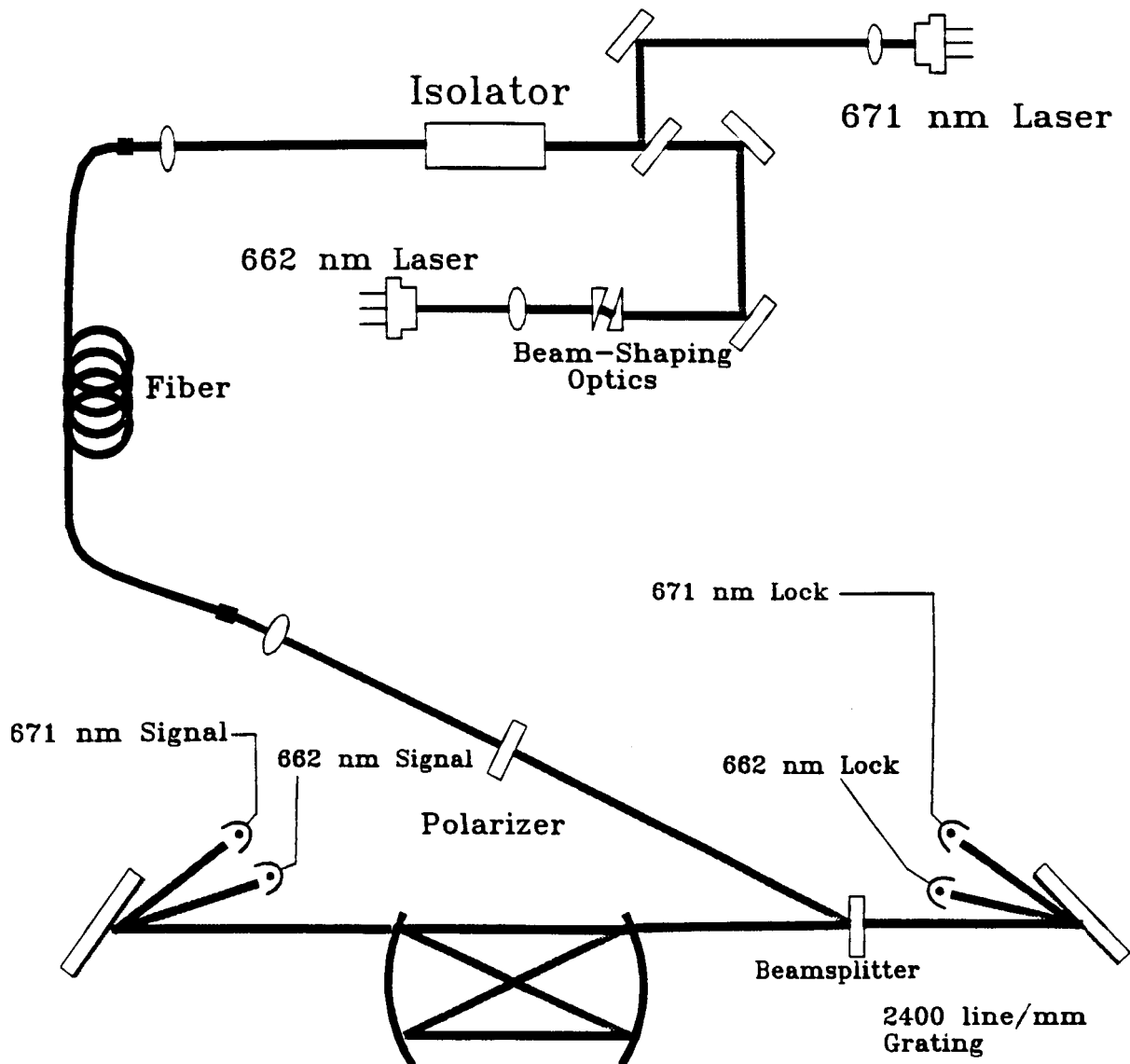
Figure 2. The system diagram. The two wavelengths are combined on the beamsplitter and coupled to a angle-polished singlemode fiber in order to spatially overlap the beams. Prior to the multipass cell, both wavelengths are intensity stabilized, by detecting each wavelength individually and feeding back to the injection currents. After the multipass cell the two wavelengths are again individually detected and the differential absorption measured. A polarizer is necessary at the fiber output to prevent changes of the beam-splitter's effective R/T ratio due to polarization changes.

V signal. The offset current drifts result in errors of the same magnitude. These outputs are switched periodically to a precision DC voltmeter, which is in turn interrogated by computer for data storage and calculation of the absorbance.

The limiting noise in absorption measurements is often due to optical etalons arising from spurious reflections between the optical components. The noise is modulated by either path length changes (vibrational) or wavelength changes. Spurious etalons that form ahead of the beamsplitter are effectively canceled by the power control servo. After the beamsplitter, etalon effects associated with

the multipass cell mirrors are the limiting noise source. A new cell with low scatter mirrors and a wedged anti-reflection coated input window is being installed, which may decrease the vibrationally induced etalon noise. In addition, experiments with a galvanometer-driven Brewster plate in the optical path after the beamsplitter are planned.

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4.0 CONCLUSION / ACKNOWLEDGEMENTS

The two-laser differential absorption technique described here may be useful for experimental situations where it is difficult to tune a laser over an absorption feature. Furthermore the approach offers a potential alternative to frequent sample removal to determine the zero absorption baseline. We thank E. Richard for discussions about signal monitoring by amplitude modulation, and K. Petrov for assistance with the Hitran96 database.

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[4] The Hitran96 molecular database is published by the Phillips Laboratory, Hanscom AFB, MA 10731-3010