High-Sensitivity Transient Spectroscopy Using Tunable Diode Lasers

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Abstract. Experimental techniques have been developed to monitor transient infrared absorptions using lead-salt tunable diode lasers. The techniques are easily implemented, yield sensitivities which are limited by detector noise at $10^{-5}$ level of absorbance, and have a response time on the order of one microsecond. The transient absorption detection techniques are high frequency versions of the sweep integration technique pioneered by Jennings [Appl. Opt. 19, 2695 (1980)]. TDL modulation rates of 100 kHz and 500 kHz allow for absorption sampling rates of 200 kHz and 1 MHz, respectively. In order to reproducibly achieve near-detector-noise-limited sensitivities for 100 kHz TDL modulation rates, an automated analog subtraction circuit has been developed which removes the effects of minor TDL power variations. At the 500 kHz modulation rate, digital filtering techniques are used to remove the effects of this power variation.

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In the past decade, lead-salt tunable diode lasers (TDL's) have been widely used for high-resolution infrared spectroscopy. Extensive research has been undertaken to enhance the sensitivity of TDL-based instrumentation. At present, infrared absorption lines with a line centre absorption of $10^{-4}$ can be detected on a routine basis. Under optimum conditions, residual noise levels equivalent to a line centre absorption of $10^{-5}$ can be achieved in gases at low pressure [1]. The combination of high sensitivity and high resolution provided by tunable diode lasers has been exploited for the detection of atmospheric pollutants and trace gases, both in the laboratory and the stratosphere [1-3]. However, the majority of the detection techniques developed to date are only suitable for the detection of a steady-state infrared absorption. Typically, the detection systems operate with time constants of the order of 1 s, and consequently cannot monitor fast changes in absorption.

In recent years, there has been increased interest in the use of tunable diode lasers to monitor transient infrared absorptions [4-6]. There are many applications where the concentration of an infrared-active constituent of a gaseous mixture changes concentration on a short time scale [7]. In a laboratory environment, transient species can often be created using a pulsed laser or a pulsed electric discharge. These species can be monitored by probing their infrared absorption spectra, provided such measurements can be made on a sufficiently fast time scale. Consequently, a variety of techniques have recently been developed to shorten the response time of TDL instrumentation, while retaining the high sensitivity. In particular, direct frequency modulation of lead-salt lasers in conjunction with heterodyne detection [8] and gated integration techniques [5] have been proposed for the sensitive detection of transient species.

In this paper, we present an alternative technique for monitoring transient infrared absorptions with TDL's. The technique is simple to implement and yields superior performance when compared with frequency modulation and gated integration techniques. Our technique is essentially a high-frequency version of the sweep integration technique pioneered by Jennings [9], and modified by Cassidy and Reid [10]. At present, we are primarily limited in sensitivity by detector noise, and a combination of better de-
tectors or more powerful lasers should directly result in improved sensitivity. Initial results describing the application of this technique for the detection of CF₂ were described by Beckwith et al. [11]. The transient detection technique has since been refined, and the response time has been shortened. We are presently able to reproducibly achieve sensitivities in the 1 × 10⁻⁵ equivalent absorbance range with an effective response time of one microsecond. To the best of our knowledge, these values of sensitivity and response time are the best reported to date.

In the next section, the experimental apparatus for the creation and detection of transient infrared absorptions is described. Sections 2 and 3 describe the experimental results for TDL modulation rates of 100 kHz and 500 kHz, respectively. Finally, a discussion and conclusions are presented in Sect. 4.

1. Experimental Apparatus

Figure 1 is a schematic diagram of the apparatus. The collimated TDL beam passes through the discharge cell and is focussed onto the HgCdTe detector. The TDL used in the present experiment can be tuned from 1200 to 1400 cm⁻¹. The demonstration of our technique required a reproducible and controlled method of generating a transient absorption line in this region. The absorption spectrum of N₂O in the 1300 cm⁻¹ region is very well known [12], and an electric discharge can be used to place a significant population into the v₃ mode of N₂O. (This excitation process is the basis of the N₂O 10 µm laser [13].) Consequently, we employed an N₂O cell in a pulsed discharge configuration to provide well-defined transient absorptions. By varying the concentration of N₂O in the gas mixture, the magnitude of the transient absorption signal could easily be controlled.

Figure 2 shows a conventional direct detection scan of room temperature N₂O in the 1273 cm⁻¹ region. The TDL was operating in a single mode with approximately 100 µW of optical power incident upon the detector. The inset of Fig. 2 indicates the transitions which create the steady-state absorption line marked “L” (used for calibration purposes) and the transition responsible for a transient absorption at 1273.527 cm⁻¹.

To attain the high modulation rates required to implement the transient detection technique, the existing TDL control electronics were modified with the addition of a conventional bias-T insertion circuit. Superimposing a sinusoidal current modulation upon the TDL bias current using this circuit causes the laser wavelength to sweep back and forth across the absorption line of interest. This wavelength modulation results in the absorption line being detected twice per cycle, and hence the absorption sampling rate is twice the TDL modulation rate. However, the current modulation also results in a modulation of the TDL optical power. Thus the detector shown in Fig. 1 responds to signals caused by both amplitude (optical power) modulation and wavelength modulation. The upper trace of Fig. 3 represents a typical signal observed at the output of the detector. Typically, the amplitude modulation has a magnitude equivalent to