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1. Introduction

The development of cw color center lasers [1] has inevitably led to their application to spectroscopy. The commercial availability of a color center laser provides ready access to this technology to any laboratory. In this paper, we wish to examine the prospects of color center lasers as tunable sources for high sensitivity infrared absorption spectroscopy, describe the development of a computer-controlled color center laser spectrometer based upon the commercial Burleigh FCL-20 laser, and report on several spectroscopic investigations using the computer-controlled color center laser.

2. Sensitivity of Absorption Spectroscopy

The sensitivity of any absorption spectroscopy experiment in terms of absorbers/unit volume is meaningless without some specification of the effective pathlength. In a laboratory experiment, the physical pathlength is generally limited by the available space, the reflectivity of mirrors in multipass optics or in some cases by the overlap of multipass beams with the consequent generation of unwanted standing waves. For some laser systems, the effective pathlength can be made very much greater than the sample length by placing the sample inside the laser cavity [2]. This length enhancement increases as the laser cavity loss is reduced and the sensitivity of laser gain to circulating power level decreases. The rate of change of gain with power level is smallest when laser action is not the dominant mechanism for the loss of population inversion. Color center lasers do not give great enhancement of effective pathlength over physical pathlength for intra-cavity absorption both because the crystals are generally fairly lossy (~5%/pass) and because they have a high quantum efficiency with laser action the dominant mechanism for loss of population inversion. Thus we will limit our sensitivity considerations to extra-cavity absorption experiments and bear in mind that there may be trade-offs between various approaches to absorption spectroscopy when the possibility of increasing the pathlength is introduced.

There are three sources of noise which could limit the minimum detectable change in laser power in absorption spectroscopy: source noise, detector noise, and quantum noise. (For further discussion of these noise sources, see SHIMODA [3]). In contrast with some other laser absorption spectroscopy experiments such as far-infrared LMR [2], color center laser

Absorption spectroscopy is dominated by source noise considerations. Color center lasers are noisy, primarily because the ion lasers which pump them are affected by acoustic vibrations, AC ripple, and noise from the instabilities in the electric discharge. Acoustic vibrations and AC ripple are dominant at low frequencies, but appear to decrease to a negligible level at a few kHz. Above a few kHz, however, noise remains essentially constant up to above 100 kHz although it should fall off above 3 MHz because the ion laser cavity acts as a tank circuit. (Here we summarize our own observations using Stark modulation of methanol and acetonitrile and an Ar⁺ laser pump. In contrast, DELEON, JONES and MUEENTER [4] report noise decreasing as 1/f to above 100 kHz using a Kr⁺ pump).

The sensitivity limitations imposed by source noise may be reduced or removed by several different approaches:

1. Reduce source noise by active amplitude stabilization (noise eaters).
2. Balance it out with two detectors (double beam compensation).
3. Balance it out by interference (balanced bridge or magnetic rotation).
4. Operate at a modulation frequency (above 3 MHz?) where source noise is reduced.
5. Increase the pathlength at the expense of power (multiple reflection cells).

Let us comment briefly about each of these options. First, noise eaters are highly effective [5] in improving sensitivity for simple absorption spectroscopy without modulation because the laser exhibits excess noise at low frequencies and regular modulation because of power line ripple. On the other hand, active feedback loops, especially those which sample the infrared beam rather than the ion laser pump, seem to be difficult to build and adjust. The second approach of using two beams and two detectors is limited by any instability in the beam direction and by drift in either detector, and ultimately by the total detector noise of the detector pair. If sophisticated signal processing, is employed slow relative drifting of the two detectors may be at least partially compensated. The third approach of interference, as realized by magnetic rotation spectroscopy, can be quite effective in reducing source noise [6]. It is limited by the quality of available polarizers and eventually by detector noise. Because S/N is increasing as $1/\sqrt{P}$ when better quality polarizers are introduced, the gain in S/N when detector noise limit is reached is far less than if the source noise were simply not present. The fourth approach of moving the modulation frequency to a value sufficiently high that noise is falling off is not easily implemented with Stark or Zeeman modulation although it remains an interesting possibility with frequency modulation. The final approach of increasing the pathlength by multiple reflection can be highly effective when sample dimensions permit especially if done in conjunction with Stark or Zeeman modulation. The S/N improves linearly with pathlength until the laser beam is attenuated to the extent that detector noise becomes a factor. This approach has been used with great success in diode laser spectroscopy by the group of HIROTA [7].

Our recent efforts have been in the direction of increased pathlength, because the signal increases linearly with pathlength. Since S/N is independent of infrared power when source noise limited, more is to be gained by increasing the pathlength at the expense of power at the detector until detector noise limited than by employing higher quality polarizers in magnetic rotation spectroscopy until detector noise limited. Recently construction of a 2 meter White Cell similar to the design of OKA [8] with

strong atmospheric water absorptions in this region, the mirrors are placed in evacuable compartments. The cell is wound with a solenoid for Zeeman modulation and an electric discharge can be maintained between the cell ends. With Zeeman modulation at 1800 Hz and detection at 3600 Hz, the minimum detectable absorption is 10^{-6} /cm (pathlength: 80 meters). The sensitivity obtained is illustrated by Fig.1 which displays the R(3) transition of OH obtained in both simple absorption and Zeeman modulation.

3. Computer Controlled Color Center Laser Spectrometer

The Burleigh FCL-20 has been converted into a computer controlled color center laser spectrometer capable of continuous single mode scans of more than 10 cm^{-1} [9]. The spectrometer is capable of acquiring extremely high resolution spectra which can be precisely measured. The system consists of the laser, diagnostics used to monitor the laser output, hardware control units for the wavelength selective elements, detectors and amplifiers for data acquisition, a CAMAC system which controls the tuning ele-

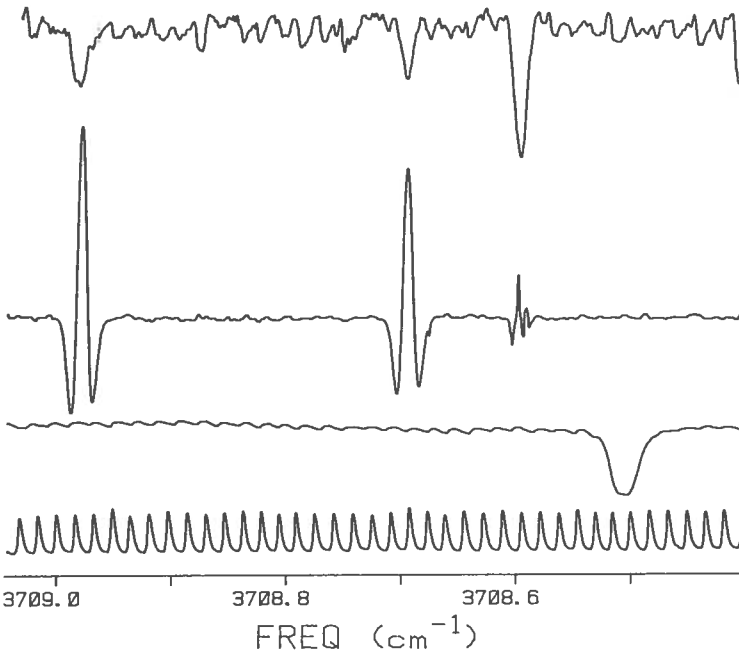


Fig.1 The R(3) transition of OH in both simple absorption (top trace) and Zeeman modulation (next trace) observed through a neon sign transformer discharge through water. The peak absorption is about 10% through an 80 m pathlength which corresponds to an OH pressure of 0.04 mTorr. Also shown: NO overtone reference spectrum and reference marker cavity. TC(Zeeman): 10 msec.

ments (grating angle, etalon length, and cavity length) and acquires the data, and DEC PDP-11/V03 microcomputer.

The method of absolute frequency calibration can be seen by examining Fig. 1. The line frequencies of the NO overtone reference spectrum are accurately known from Fourier transform spectroscopy. The temperature compensated Invar reference cavity has been observed to be stable to 0.001 m^{-1} for several hours. A feature can thus be measured with a precision of 0.0003 cm^{-1} and an accuracy of $\sim 0.001 \text{ cm}^{-1}$. A detailed description of the spectrometer can be found elsewhere [9].

1. Spectroscopic Studies

Several spectroscopic investigations have been carried out using computer controlled color center lasers. The fundamental vibration of OH has been observed by magnetic rotation spectroscopy [6] in the products of a microwave discharge in water. The magnetic dipole allowed transition between the fine structure levels of the Br atom has been observed using magnetic rotation [10]. This transition had been observed in emission with very high resolution by Fourier transform spectroscopy [11]. However, the resolution obtainable by color center laser spectroscopy was sufficient to resolve completely the isotopic structure which was incompletely resolved in the Fourier transform study. The isotopic mass shift in the fine structure transition frequency was determined by color center laser spectroscopy to be 14 MHz.

The spectra of two stable molecules, nitrogen dioxide and methanol, have been investigated with the color center laser spectrometer. In the case of nitrogen dioxide the transition observed is the combination band $(1,1,1) \leftarrow (0,0,0)$, while for methanol the OH stretch fundamental has been studied. These investigations will be reported elsewhere.

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