High Sensitivity Color Center Laser Spectroscopy

R.F. Curl, Jr., J.V.V. Kasper, P.G. Carrick, E. Koester, and F.K. Tittel

Departments of Chemistry and Electrical Engineering and Rice Quantum Institute, Rice University, Houston, TX 77001, USA

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

A. R. W. McKellar et al. (eds.), *Laser Spectroscopy V*

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 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 MUENTER [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