

Color-Center Laser Spectroscopy of Small Free Radicals

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Abstract

The application of CW color-center lasers to the study of absorption spectra of small free radicals in the wavelength region from 0.8 to 3.3 μm is described. The laser spectrometer has been tested on the vibrational overtone band of NO at 2.68 μm and the fundamental vibrational spectrum of OH in absorption. Zeeman-modulation and magnetic-rotation spectroscopy have been used to reduce the effects of source noise and improve spectroscopic sensitivity.

INTRODUCTION

The recent development of tunable single-frequency CW color-center lasers with a wavelength coverage from 0.8 to 3.3 μm ^(1,2) opens new possibilities for investiga-

tion of molecular species in the near infrared. Of special interest is the detection and characterization of small free-radical species by means of high-sensitivity, high-resolution absorption spectroscopy. The spectroscopy of free radicals is of interest for several reasons. First, these species are intermediates in many chemical processes such as the combustion of hydrocarbons. Because of their high reactivity, the development of high-sensitivity techniques to detect and monitor these intermediates presents an important and challenging problem. Second, the analysis of such spectra of the CH, OH, NH, and FH bond-stretch fundamentals near $3\ \mu\text{m}$ provides valuable structural information. A third incentive for carrying out these studies is that the presence of free radicals in interstellar clouds is known from radio-astronomical observations, and the observation and analysis of the infrared spectra of new free radicals can provide transition frequencies for radio-astronomy searches.

The color-center laser (CCL) has all the desirable characteristics for spectroscopic applications in the near infrared⁽¹⁾ that the dye laser has in the visible. The tuning range of an individual color-center crystal is typically several hundred nanometers, and single-frequency operation with a free-running linewidth of much less than 1 MHz can be achieved. CW output powers are on the order of 50 mW. Other presently available sources of tunable infrared radiation either have considerably less output power (diode lasers,⁽³⁾ CW difference-frequency generation,⁽⁴⁾ operate in a pulsed mode with broad linewidths (parametric oscillators,⁽⁵⁾ Raman sources), or are not yet readily available (transition-metal-doped solid-state lasers).

In this paper we describe the operation of CCL spectrometers that utilize the linear cavity configuration. (We have operated CCLs in the ring cavity configuration and intend to develop a CCL spectrometer with a ring cavity.) Computer control makes possible single-frequency scans of up to $100\ \text{cm}^{-1}$ with a resolution determined by the cavity mode spacing (250 MHz), and continuous high-resolution scans (linewidth below 1 MHz) over 1-cm^{-1} ranges. The performance of the IR laser spectrometer has been evaluated on the first overtone band of NO at $2.68\ \mu\text{m}$. In the case of absorption spectroscopy using CCLs, the sensitivity is limited by amplitude fluctuations, mainly due to the pump-laser noise. Experimental techniques for the reduction of this source of noise, in particular magnetic-rotation spectroscopy, have been developed and will be discussed. As an example of evaluating the utility of this new technique for the detection of low steady-state concentrations of free radicals, the fundamental vibrational spectrum of OH was observed.

EXPERIMENTAL ARRANGEMENT

A tunable CW CCL spectrometer is shown schematically in Fig. 1. It consists of a krypton or argon ion pump laser, the color-center laser, and diagnostic instrumentation. The CCL utilizes an astigmatically compensated, collinearly pumped three-mirror cavity design as in the Burleigh commercial FCL laser and others described in the literature.^(1,2,6) The CCL is tuned by appropriate adjustment of three elements: a Littrow-mounted diffraction grating, an air-spaced etalon, and a PZT-mounted folding mirror or tilted scan plate. The grating functions as both tuning element and output coupler.⁽⁷⁾ The zero-order reflection couples 20% of the power

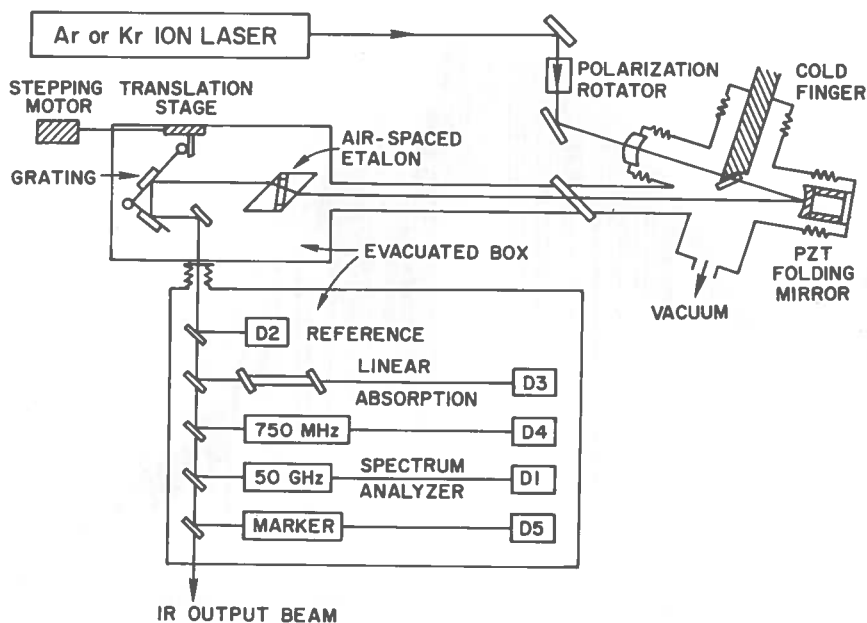


Figure 1. Schematic for computer-controlled CW color-center-laser spectrometer.

out of the cavity. With the etalon removed from the cavity, the laser operates in two longitudinal modes which are separated in frequency by 4.17 GHz. This two-mode operation results from the spatial hole-burning effect in the standing-wave cavity.⁽⁸⁾ Coarse-resolution (0.1-cm^{-1}) survey scans can be made in this configuration for rapid mapping of a spectrum. Insertion of an air-spaced etalon with free spectral range (FSR) of 25.3 GHz and 30% reflective coating gives stable single-mode operation with a linewidth of less than 1 MHz. Scanning only the etalon, the laser can be tuned in cavity-mode steps of 250 MHz (0.01 cm^{-1}) over a range of about 20 GHz. To achieve continuous narrow-line tuning, the cavity length must be adjusted by concurrently tracking the folding mirror or tilting an intracavity scan plate.

The CCL crystal is cooled cryogenically by means of a copper cold finger to 77 K for high optical gain and quantum efficiency and long crystal lifetime. This requires a good vacuum ($<10^{-5}$ torr) for good thermal isolation of the crystal. Because of the strength of many atmospheric absorption lines in this wavelength region (Fig. 2), a fairly good vacuum (<10 mtorr) throughout the laser cavity is required for smooth laser tuning.

To date for this particular laser, we have used $\text{KCl}:\text{Li}$ and $\text{RbCl}:\text{Li}$ crystals with $F_A(11)$ centers in the wavelength range from 2.3 to $3.2\ \mu\text{m}$. However, the operating region of the CCL spectrometer can be extended by the use of other color-center crystals.^(1,2)

In order to monitor single-frequency operation and tuning, portions of the laser output are directed to two spectrum analyzers (FSR = 750 MHz and 50 GHz) and a stable marker cavity (FSR = 500 MHz) as shown in Fig. 1. Strong variations of the

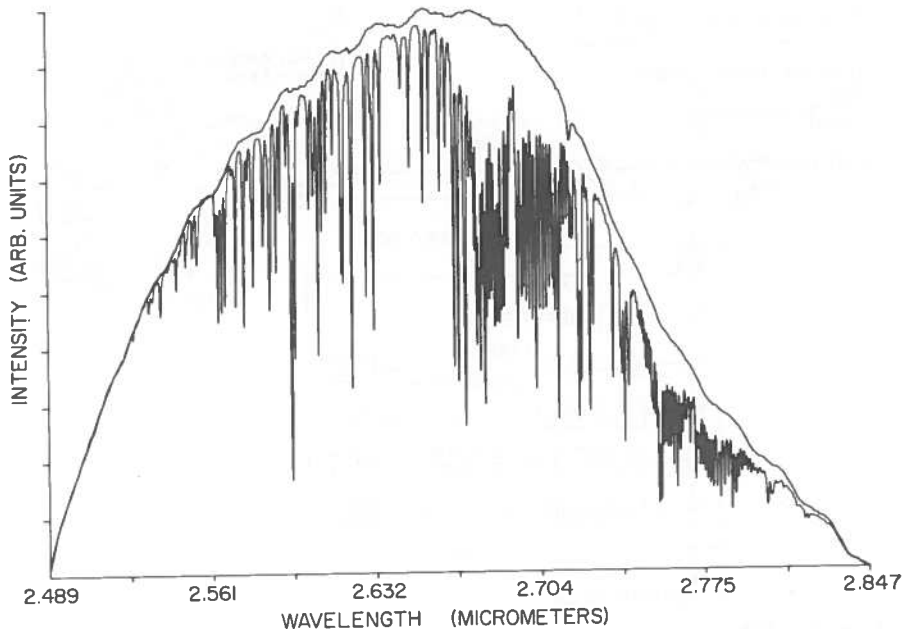


Figure 2. Typical power spectrum of KCl:Li color-center laser, with and without modulation of H₂O absorption.

fineness of these instruments caused by atmospheric absorption lines are also prevented by use of an evacuated chamber. For wavelength calibration a 30-cm sample cell containing a gas with a well-known spectrum, and a reference detector monitoring the laser power, are used. All infrared signals are observed with lead sulfide detectors covered by germanium windows. The remaining output power (60%) is available for the experiment.

The spectrometer is interfaced to a Digital Equipment Corporation (DEC) LS1-11 minicomputer using various CAMAC modules and a Kinetic Systems 3912 controller.^(6,9) The computer tunes the laser in open-loop operation by synchronously adjusting the grating angle, etalon separation, and cavity length at the proper rates. A stepping motor, driven by a BiRa 3101 driver, rotates the grating via a sine drive. The position of the motor relative to a fixed limit switch thus determines the grating angle. The air-spaced etalon and PZT-mounted mirror are controlled by high-voltage amplifiers, which are driven by appropriate voltages from a Kinetic Systems 3112 digital-to-analog converter. Data from the various signals are acquired via a BiRa 4301 analog-to-digital converter. Both the 60-Hz line frequency and an SEC RTC-01 real-time clock are used for timing the data acquisition and scanning.

OPERATION AND PERFORMANCE

In order to continuously scan the frequency of a CCL, three tuning elements must be tracked synchronously. These are the grating angle (which determines the ap-

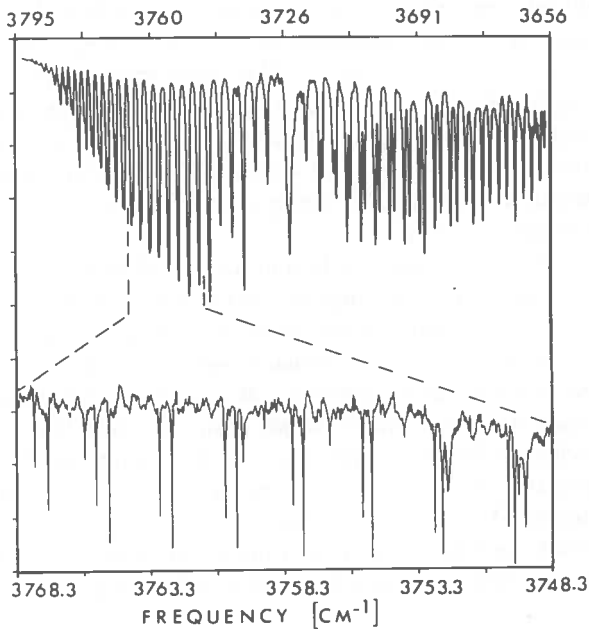
proximate frequency region), the etalon spacing (which selects the particular single mode of the laser cavity that oscillates), and the cavity length (which determines the exact frequency of laser oscillation). The etalon spacing and cavity length are usually swept by applying a voltage ramp to a PZT. The grating angle is usually swept with a small motor through a sine drive. To achieve proper tuning, the computer uses cross-reference tables which correlate the position of each tuning element to wavelength or frequency. Scanning is accomplished by incrementing each tuning element at the proper rate.

There are two major problems involved in tracking these elements to obtain long single-frequency scans. First, the range of voltage which can be applied to the PZT elements without electrical breakdown is not sufficiently great to scan the wide regions desired. Therefore, a ratcheting scheme must be employed in which the PZT ramp is stopped with the output frequency at a particular value and then the PZT voltage is set back to a lower value, which brings in a new laser cavity or etalon mode that coincides in frequency with the previous stopping point. This ratcheting process is complicated by the second problem, which arises from the fact that the frequency determined by a PZT is not linear in the voltage applied to it. Thus the frequency at which the CCL oscillates is a fairly complicated function of the three control variables: grating motor position, etalon PZT voltage, and laser-cavity PZT voltage.

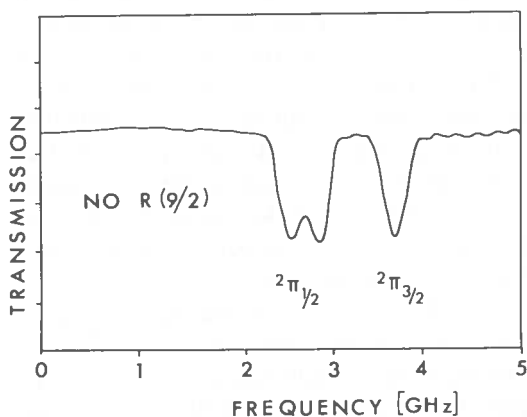
Low-resolution scans with a linewidth of 0.1 cm^{-1} can be made by scanning only the grating, with the etalon removed from the cavity. The upper traces of Fig. 3a shows as an example a low-resolution scan of the overtone 2-0 absorption band of NO. Long-range single mode scans can be made by scanning both the etalon and the grating. The computer automatically sets the etalon back after it has scanned one FSR, followed by a suitable delay (typically 2 sec) to allow transient ringing and drift to decay before resumption of scanning. In this manner, scans of up to 100 cm^{-1} have been made with a resolution of 250 MHz (0.01 cm^{-1}), as determined by the cavity mode spacing. The lower trace of Fig. 3a shows a high-resolution scan of a 20-cm^{-1} segment of the R-branch of NO. For different rotational quantum numbers, pairs of absorption lines belonging to the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ transitions are clearly resolved. Due to impurities in our NO sample, additional lines appear, which probably arise from H_2O absorptions.

The cross-reference table for the etalon spacing must be periodically updated (generally once a day when starting), due to drift in the HV amplifier and in etalon temperature. This proved to be a simple matter of an additive shift of the entries in the table. The magnitude of the shift is that needed for the most stable single-mode operation as observed on the spectrum analyzers. Once it is set, long-range single-mode scans can be routinely made without further adjustment.

Smooth single-mode scans without cavity-mode jumps are made by additionally tracking the cavity length. This is done with the PZT-controlled folding mirror, which is repetitively scanned and set back by the computer, again with suitable delay for settling. The technique for controlling the cavity length is the same as described above for the etalon. Figure 3b shows such a high-resolution scan of the $\text{R}(\frac{9}{2})$ line of NO. The Λ -doubling of the $^2\Pi_{1/2}$ transition with a separation between the two peaks of $305 \text{ MHz}^{(10)}$ is clearly resolved. The resolution of this measure-



(a)



(b)

Figure 3. Absorption spectrum of the 2-0 overtone of NO at 2.68 μm . (a) Upper trace: low-resolution scan using only the grating as tuning element, taken with a pressure of 500 torr. Lower trace: Scan with cavity mode resolution at 40-torr NO pressure. The $R(\frac{27}{2})$ to $R(\frac{13}{2})$ lines are displayed. Additional lines are due to water impurities. (b) Continuous single-mode scan over the $R(\frac{9}{2})$ transition with 5-torr NO pressure. Both ${}^2\Pi_{1/2}$ and ${}^2\Pi_{3/2}$ transitions are observed, with the ${}^2\Pi_{1/2}$ transition split by Λ -doubling.

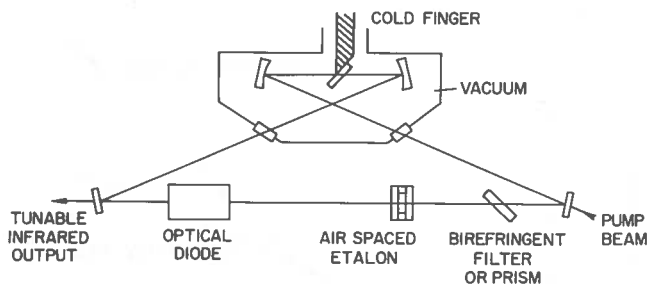


Figure 4. Ring color-center laser.

ment is limited by the Doppler broadening, which is significantly wider than the spectrometer linewidth.

An alternative resonator configuration for the CCL spectrometer is a ring-resonator geometry. Such a traveling-wave cavity eliminates the spatial hole-burning effect associated with the linear resonator and results in high single-frequency output powers similar to those of the dye ring laser.⁽⁹⁾ Such a laser arrangement is shown in Fig. 4. So far, using a LiF F_2^+ -color-center crystal in excess of 1 W in single-frequency and unidirectional operation has been achieved in the near infrared from 0.86 to 1.04 μm . This cavity configuration should be quite suitable for computer-controlled operation as a spectrometer.

SENSITIVITY CONSIDERATION AND IMPROVEMENT

Besides the high-resolution scanning capability of the CCL spectrometer discussed in the previous section, the development of high-sensitivity absorption methods is essential. Over the past few years, a number of new, high-sensitivity spectroscopic methods using lasers have been developed. The unique properties of lasers can be utilized to provide a variety of powerful detection methods involving fluorescence, photofragmentation, photoionization, or acoustic detection. However, the environment in which many molecular species of interest are found often makes absorption spectroscopy the most attractive method of detection.

Let us define the absorption signal as the difference between the power reaching the detector without the sample absorption and that reaching the detector with sample absorption. For a small fractional absorption,

$$S = \Delta P = \alpha LP$$

where α is the absorption coefficient, L is the effective pathlength, and P is the power reaching the detector. The sensitivity is determined by the requirement that the signal-to-noise ratio (S/N) be greater than unity so that in order to estimate and improve the sensitivity, the sources of noise must be considered. There are three kinds of noise, which have different dependence on the power reaching the detector

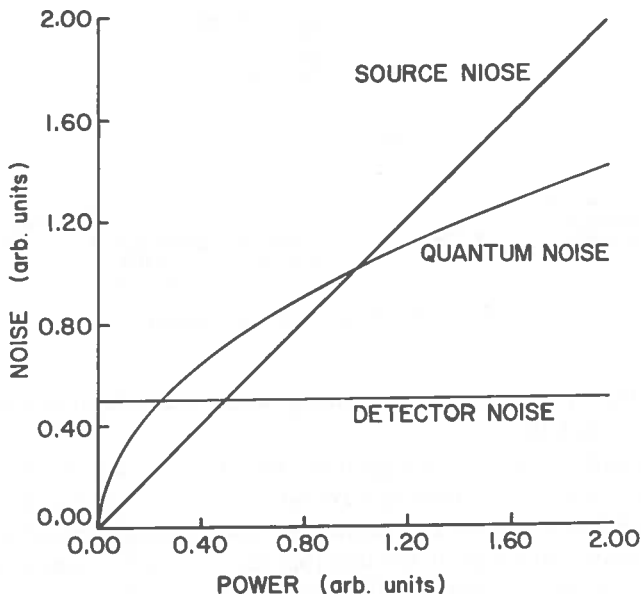


Figure 5. Noise characteristics.

(see Fig. 5), source noise, detector noise, and quantum noise. Source noise arises from the amplitude fluctuations in the laser, which are due to a number of physical sources such as mechanical vibrations, plasma noise in the pump laser, and ripple in the power supplies. It is proportional to the infrared power. Detector noise arises in the detector from Johnson noise in detector viewed as a resistor, thermal generation of charge carriers, and so on. The detector noise determines the minimum detectable infrared power, but is independent of the infrared power and is an unimportant source of noise at high infrared powers. Quantum noise arises because photons are discrete particles and are detected in discrete events, which exhibit statistical fluctuations. Quantum noise is proportional to the square root of the power. If conditions can be adjusted so that the source noise and detector noise are less than the quantum noise, then the quantum noise provides a theoretical limit to the sensitivity.

Sensitivity, in terms of molecules/cm³, depends, of course, on the transition moment and the partition function. For the OH radical, as an example, the quantum noise limit (see below) for a pathlength of ≈ 20 cm corresponds to a sensitivity of $\approx 10^8$ molecules/cm³. Unfortunately, CCLs exhibit considerable amplitude fluctuations or source noise, primarily arising from noise in the ion lasers used to pump them. If no effort is made to reduce the effects of source noise, the observed sensitivity for OH is about 10^{13} – 10^{14} molecules/cm³. It therefore is essential for high sensitivity to eliminate or defeat this source noise. In principle this is always possible, but the development of practical schemes raises technical problems which must be overcome.

There are three possible approaches to overcoming the sensitivity limitations imposed by amplitude fluctuations of the laser:

1. An active laser amplitude stabilization scheme may be developed which greatly reduces the amplitude fluctuations.⁽¹¹⁾
2. Balancing or compensating schemes may be developed in which the amplitude instabilities are still present but their interference with absorption spectroscopy is reduced.⁽¹²⁾
3. The absorption signal may be detected at a modulation frequency (>100 kHz) for which the laser noise power spectrum has a very low amplitude.

So far we have investigated the reduction of source noise using magnetic-rotation spectroscopy.⁽¹²⁾ This technique is a balancing scheme belonging to category 2 above. The magnetic-rotation method has the advantage of selecting absorption signals of paramagnetic molecules, thereby eliminating background absorption from diamagnetic species. By combining active amplitude stabilization with magnetic rotation, even higher sensitivities can be obtained.

A vibrational transition in a paramagnetic species is to be considered. As the simplest case it is supposed that the g -factor is unaffected by the vibration and that $\Delta J = 0$ (Q -branch). In the presence of a magnetic field along the direction of propagation, the transition splits symmetrically into a $\Delta M = +1$ and a $\Delta M = -1$ component, with the former absorbing only right-hand circularly polarized light (see Fig. 6). As a light beam, originally linearly polarized, propagates through the sample, the polarization becomes elliptical due to preferential absorption of one circular component, and the axis of polarization rotates because the two circular components have different refractive indices. If a nearly crossed polarizer is placed in the beam after the sample, the rotation of the polarization axis can be detected.

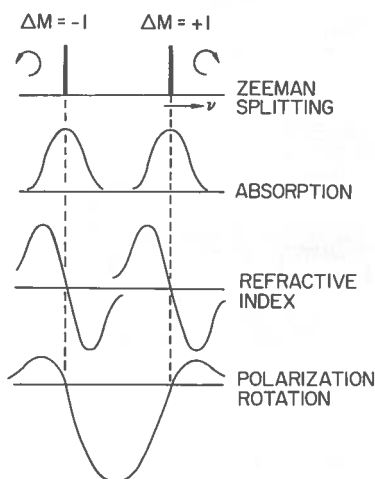


Figure 6. Principle of magnetic-rotation spectroscopy.

Under the optimum nearly-crossed-polarizer operating conditions, the signal resulting from the polarization rotation is proportional to the square root of the power reaching the detector, while the source noise is directly proportional to this power. Thus, as the polarizer is rotated towards extinction, S/N is proportional to the inverse square root of the transmitted power and is increasing. This S/N improvement is limited either by the fact that the polarizers have a finite extinction ratio or by detector (or rarely, quantum) noise.

The experimental arrangement for magnetic-rotation spectroscopy is shown in Fig. 7. Two polarizers are used to ensure that the output of the laser is linearly polarized. The polarizers are MgF₂ Rochon prisms and have an extinction ratio of $\approx 10^{-3}$. The air-cooled solenoid was usually driven at 216 Hz and 4-Å peak current, providing a peak field of ≈ 450 G. The pathlength modulated by the solenoid is ≈ 20 cm. The detector noise of the room-temperature PbS detector was found to be negligible in comparison with source noise with the polarizers crossed, so that the sensitivity is still source-noise limited.

The system was tested by observing the first overtone band of NO at 2.7 μm . Some years ago, studies were made of the magnetic-rotation spectrum of this band⁽¹³⁾ and of the fundamental,⁽¹⁴⁾ using blackbody sources. The absorption coefficients of the individual rotational components of this band were recently measured by difference-frequency laser spectroscopy.⁽¹⁰⁾ It is thus possible to obtain both relative (by comparison with simple absorption and Zeeman-modulation spectroscopy) and absolute measurements of the sensitivity of the magnetic-rotation technique.

Figure 8 shows a comparison of the $Q(\frac{3}{2})^2 \Pi_{3/2}$ signal for magnetic rotation and simple Zeeman modulation. It is clear that the improvement in sensitivity using magnetic rotation is considerable. Using the known absorption coefficients,⁽¹⁰⁾ the minimum detectable peak absorption coefficient can be estimated as 10^{-5} cm^{-1} .

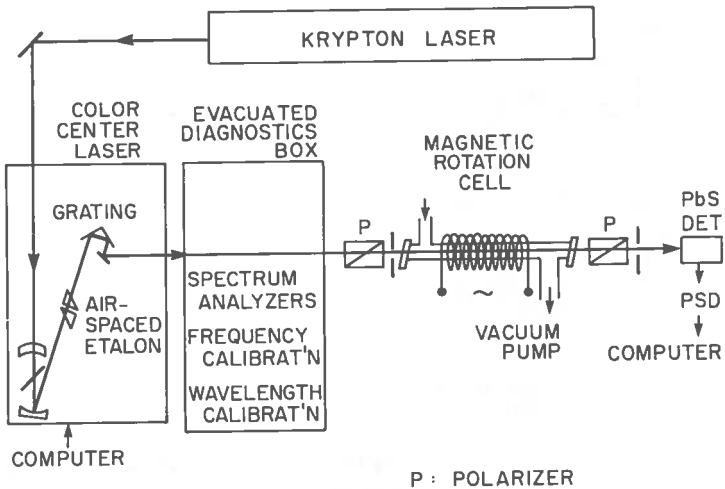


Figure 7. Experimental arrangement for magnetic-rotation spectroscopy.

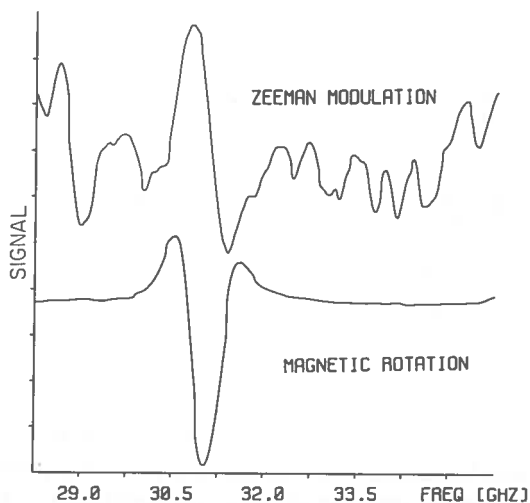


Figure 8. Comparison of the signals for magnetic rotation and simple Zeeman modulation under the same conditions for the $Q(\frac{3}{2})^2\Pi_{3/2}$ line of the $\nu = 2-0$ transition of NO.

Because of spin uncoupling, both $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ levels can be Zeeman modulated. Such a magnetic-rotation spectrum is shown in Fig. 9. The splitting of the $^2\Pi_{1/2}$ transition is due to Δ -doubling. The $^2\Pi_{3/2}$ R-branch phase is inverted in comparison with the $^2\Pi_{3/2}$ Q-branch because the frequency shifts of the strong Zeeman components are dominated by the difference in g -factors between the upper and lower states and not the change in M .

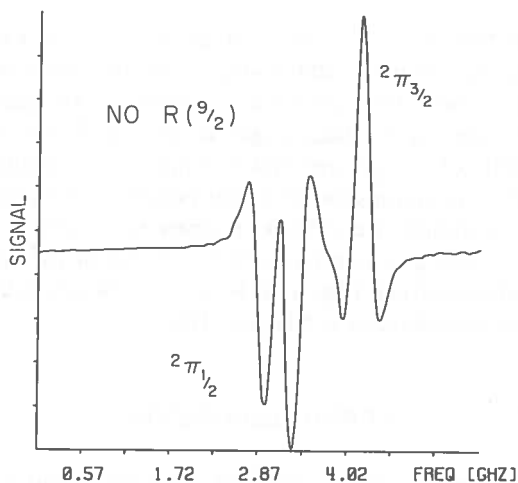


Figure 9. A typical portion of the NO spectrum in magnetic rotation showing both $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ transitions.

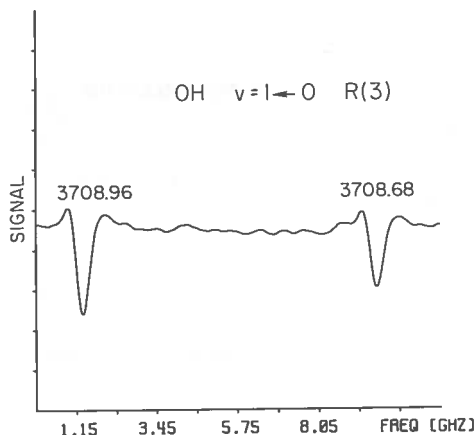


Figure 10. The two Λ -doubling components of OH $\nu=1-0$ R(3) F_1 observed in the products of a microwave discharge in water. The pathlength is 20 cm.

As a test of the utility of the system for the detection of free-radical species, the fundamental vibrational spectrum of OH was observed by pumping the products of a microwave discharge in water through the cell. The two Λ -doubling components of the R(3) F_1 transition are shown in Fig. 10. This is the first observation of this spectrum in absorption. With the same experimental conditions, these signals cannot be observed by simple Zeeman modulation. The observed wavenumber positions of these lines are in excellent agreement with the emission-spectrum study.⁽¹⁵⁾

CONCLUSION

In summary, it has been shown that the color-center laser is an excellent source for spectroscopy in the near infrared, embodying all the desirable characteristics that a dye laser possesses in the visible. The CCL is capable of extremely high-resolution, high-sensitivity spectroscopy by using magnetic rotation. In the future, we plan to improve the sensitivity of the spectrometer by employing amplitude stabilization of the output and either a combination of better polarizers or a multipass absorption cell. In this manner it should be possible to improve the sensitivity from 10^{12} molecules/cm² to close to the quantum noise limit of between 10^8 and 10^9 molecules/cm². Presently, high-resolution, high-sensitivity spectroscopic efforts are underway to detect several free radicals such as NH₂ and HO₂.

ACKNOWLEDGMENTS

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