Sensitivity enhancement of laser absorption spectroscopy by magnetic rotation effect

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(Received 28 January 1980; accepted 26 February 1980)

The use of magnetic rotation spectroscopy (Faraday effect) to reduce the effects of source noise and improve sensitivity of spectroscopy with color center lasers has been analyzed theoretically and tested experimentally on the vibrational overtone band of NO. Sensitivity improvement of a factor of 30 compared with simple Zeeman modulation has been demonstrated. As an example of this technique, the first observation of the fundamental vibrational band of the OH radical in absorption is reported.

There is an obvious need for more sensitive spectroscopic techniques to detect, monitor, and characterize many species such as free radicals and ions which generally have low steady state concentrations. 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 nature of the environment in which many species of interest are found often makes absorption spectroscopy the most attractive method of detection.

The limiting sensitivity of laser absorption spectroscopy has been examined by Shimoda.[1] He demonstrated that for pathlengths of less than a meter and moderate laser powers about 10^8 molecules/cm^3 could be detected for light molecules and a reasonable transition dipole moment. Such sensitivities have indeed been achieved in far-infrared laser magnetic resonance spectroscopy (LMR),[2,3] and nearly as high sensitivities ($\sim 10^9$) have been achieved in mid-infrared LMR.[4] The lasers employed in these experiments are very quiet and the limiting noise is very close to the quantum or maser noise limit.

However, LMR has the disadvantage that the experiments are carried out by tuning the molecular transitions into resonance with the fixed frequency laser by application of an external magnetic field. Simple absorption spectroscopy using a tunable laser which requires no near coincidence or strong magnetic tuning field obviously offers many advantages. While excellent sensitivity with a tunable source has been demonstrated[5] using a spin–flip Raman laser, some of the best tunable lasers from the point of view of ease of operation, broad tunability, and good output power, cw dye and color center lasers, have much higher amplitude fluctuations. This source noise appears to arise primarily from the amplitude fluctuations of the pumping ion laser.[6]

Although active amplitude stabilization schemes[7] can substantially reduce the noise of an ion laser beam, the stabilization required to reach the quantum noise limit corresponds to a noise reduction of about 10^7. It is unlikely that active stabilization devices of such high performance will be constructed in the near future.

In the work reported here a somewhat different approach to the reduction of source noise using magnetic rotation spectroscopy has been developed. 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.

REDUCTION OF SOURCE NOISE

The three basic sources of noise in an absorption spectroscopy experiment are source noise, detector noise, and quantum noise. Source noise results from amplitude fluctuations of the source intensity. These amplitude fluctuations arise from a variety of physical causes such as power line ripple, acoustic vibrations, and plasma noise. Since source noise limits the sensitivity of simple absorption spectroscopy with cw color center and dye lasers, its reduction is of primary interest here. If the source noise is reduced sufficiently by the method to be described, either of the other two noise sources mentioned above may limit the maximum sensitivity.

The reduction of source noise by balanced bridge techniques is well known in rf and microwave spectroscopy.[8] The interferometer scheme for saturation spectroscopy with cw dye lasers developed by Kowalski, Hill, and Schawlow[9] is exactly analogous. Because of the technical problems associated with maintaining interferometer balance in many systems of interest (flowing gas streams and electrical discharges), and because of the difficulties associated with modulating the absorption in one arm of the interferometer but not the other, the magnetic rotation of polarization as a means of reducing source noise was adopted here. This scheme is closely related to the polarization saturation spectroscopy technique developed by Hänsch[10] but is much easier to analyze theoretically, since saturation

 0021-9606/80/126602-04$01.00

is not involved. We have recently learned that Takami and Kakimoto[11] have been developing the same approach as is being described here in order to reduce source noise in cw dye laser absorption spectroscopy.

THEORY

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. 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.

The theoretical analysis of the signal passing through the polarizer is straightforward. Assume that the angle between the nearly crossed polarizers is $\varphi + \pi/2$, thus making φ small. The angle is measured in the direction of right hand rotation looking down the beam. Further assume for the moment that both polarizers are ideal, i.e., the light reaching the detector is zero when $\varphi = 0$. The linearly polarized light emerging from the first polarizer can be decomposed into two equal amplitude right-handed and left-handed circularly polarized waves which will have different complex propagation constants for the electric field in the medium because of the Zeeman splittings caused by the axial magnetic field, since the right hand circularly polarized wave has absorptions with $\Delta M = +1$ and the left hand has $\Delta M = -1$. After passing through the sample, the vector component of the electric field in the direction passed by the second polarizer can be computed by recombining the two circularly polarized components, which will now have different amplitudes and will have experienced different phase shifts. By computing the time average of the square of the electric field for the light emerging from the second polarizer, the power can be calculated, giving the result

$$P(\varphi) = (P_0/2)\exp(-2I_A L)\left[\cosh(I_\Delta L) - \cos(R_\Delta L + 2\varphi)\right], \tag{1}$$

where $P(\varphi)$ is the power passed through the polarizer after the sample which is oriented at an angle $\varphi + \pi/2$ with respect to the incident plane of polarization, P_0 is the power incident on the sample, I_A is the average attenuation of the fields of the two circular waves, L is the path length, I_Δ is the difference in the attenuation of the fields of the two circular waves (RHCP – LHCP), and R_Δ is the difference in the real parts of the field propagation constants for the two circular polarizations (again RHCP – LHCP). For a weak absorption line and small φ (nearly crossed polarizer), Eq. (1) reduces to

$$P(\varphi) = (P_0/2)\left[(1 - \cos 2\varphi) + R_\Delta L \sin 2\varphi\right] \tag{2}$$

neglecting terms in the square of the propagation constants and assuming that the polarizers will not be exactly crossed.

In the absence of the magnetic field R_Δ is zero. With the field on, the $\Delta M = +1$ and $\Delta M = -1$ components are separated in frequency by $2g\beta H$, and R_Δ is the difference between two terms each of which is given by

$$R_\pm = (|\mu_{ij}|^2/2u\hbar\epsilon_0)(N_1 - N_2)\,\mathrm{Re}Z[(\Delta\nu_\pm + i\Delta)\lambda/u], \tag{3}$$

where μ_{ij} is the transition dipole moment, $u[= (2kT/m)^{1/2}]$ is the most probable velocity, N_1 and N_2 are the lower and upper state particle densities of the two levels ($/\mathrm{cm}^3$), Z is the plasma dispersion function,[12] $\Delta\nu_\pm$ ($= \nu - \nu_0 \mp g\beta H$) is the frequency displacement from the peak absorption of the component, Δ is the homogeneous linewidth, and λ is the laser wavelength.

The plasma dispersion function is given by

$$Z(\zeta) = \pi^{-1/2}\int_{-\infty}^{+\infty} dx \exp(-x^2)/(x - \zeta), \tag{4}$$

where ζ is complex and $Im\,\zeta > 0$ and arises in this problem when the homogeneously broadened complex electric field propagation constants

$$k = \left(\frac{2\pi\nu}{c}\right) + \left(\frac{|\mu_{ij}|^2\nu}{2\hbar c\epsilon_0}\right)\frac{(N_1 - N_2)}{(\nu_0 - \nu) - i\Delta} \tag{5}$$

are averaged over the Doppler distribution of ν_0's

$$f(\nu_0) = \frac{\lambda}{u\sqrt{\pi}}\exp\left[-\left(\frac{(\nu_0 - \nu_{ij})\lambda}{u}\right)^2\right], \tag{6}$$

where ν_{ij} is the center frequency of the Doppler broadened line.

By employing an alternating magnetic field,

$$H = H_0 \sin 2\pi f t, \tag{7}$$

and thereby modulating the molecular absorption, baseline drift due to drift in the laser intensity can be eliminated. The line shape expected can be calculated by substituting (7) into (3) and (3) into (2) and calculating the Fourier component of the signal at the modulation frequency, f, by numerical integration to obtain the expected signal from a PSD tuned to f. The predicted line shapes are shown in Fig. 1.

The expected source noise reduction can be estimated from Eq. (2) by noting that the expected transmitted power is given by $P_T = P_0(1 - \cos 2\varphi)/2$, and therefore the signal can be written as

$$S = (P_T P_0)^{1/2} R_\Delta L. \tag{8}$$

Defining the extinction ratio of the polarizer as ξ, and following the analysis of Hänsch,[8] the maximum reduction in source noise is found when the polarizer is deliberately offset so that the total transmitted light is $2\xi P_0$. The signal to transmitted power ratio is given by

$$S/P = R_\Delta L/2(\xi)^{1/2} \tag{9}$$

In our experiments the sensitivity is limited by the polarizer extinction ratio, ξ. However, with a greatly improved polarizer, the sensitivity may be limited either by detector noise or even possibly by quantum noise. Suppose that the polarizer is nearly crossed but ξP_0 is

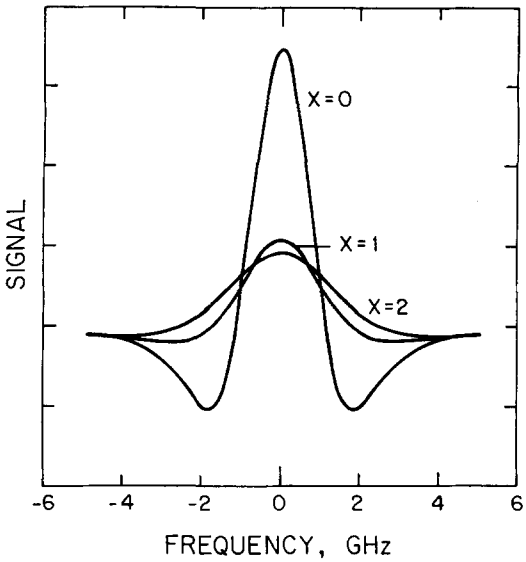

FIG. 1. Calculated line shapes for modulated magnetic rotation spectroscopy. Three ratios of homogeneous to Doppler widths are used corresponding to $x = \lambda\Delta/u$ of 0, 1, and 2. The vertical scale has been increased by two between $x = 1$ and $x = 2$ as it would be if the concentration increased with pressure. The concentration for $x = 0$ is assumed to be the same as $x = 1$. The assumed $1/e$ Doppler half-width is 1 GHz.

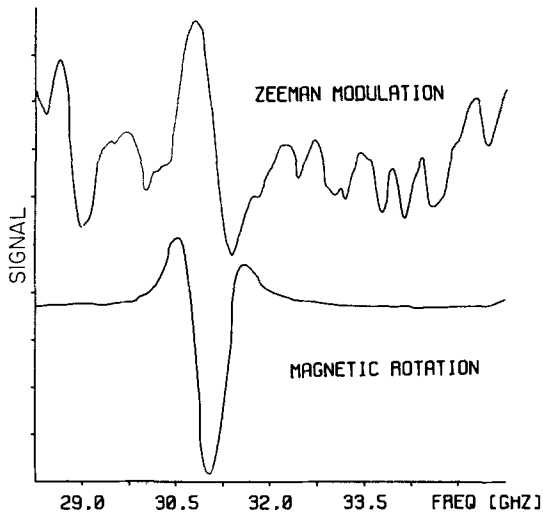

FIG. 3. Comparison of the signals for magnetic rotation and simple Zeeman modulation under the same conditions for the $Q(3/2)\ ^2\Pi_{3/2}$ line of the $v = 2 \leftarrow 0$ of NO.

still negligible in comparison with P_T, then as the polarizer is crossed further, the signal decreases as the square root of the transmitted power, the source noise linearly with transmitted power, detector noise is independent of transmitted power, and quantum noise decreases as the square root of transmitted power. Thus, as the polarizer is crossed further, signal-to-source noise is increasing as the inverse square root of the transmitted power, signal-to-detector noise is decreasing as the square root of the transmitted power, and signal-to-quantum noise is independent of the transmitted power. Either detector noise or quantum noise may limit the ultimate sensitivity, although the detector noise is more likely to be limiting unless the laser power is quite high or the detector NEP is very low.

EXPERIMENTAL

The experimental arrangement is shown in Fig. 2. The computer controlled single mode color center laser, based on a previous design,[6] will be described elsewhere.[13] Two polarizers are used to insure that the output of the laser is linearly polarized. The polarizers are MgF_2 Rochon prisms and have an extinction ratio of $\sim 10^{-3}$. The air-cooled solenoid was usually driven at 216 Hz and 4 A 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 to source noise with the polarizers crossed so that sensitivity is still source noise limited.

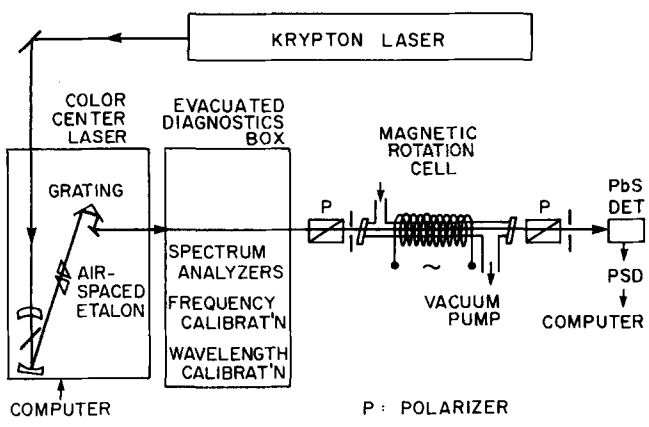

FIG. 2. Experimental arrangement.

RESULTS

The system was tested by observing the first overtone band of NO at 2.7 μ. Some years ago, studies were made of the magnetic rotation spectrum of this band[14] and of the fundamental[15] using blackbody sources. The absorption coefficients of the individual rotational com-

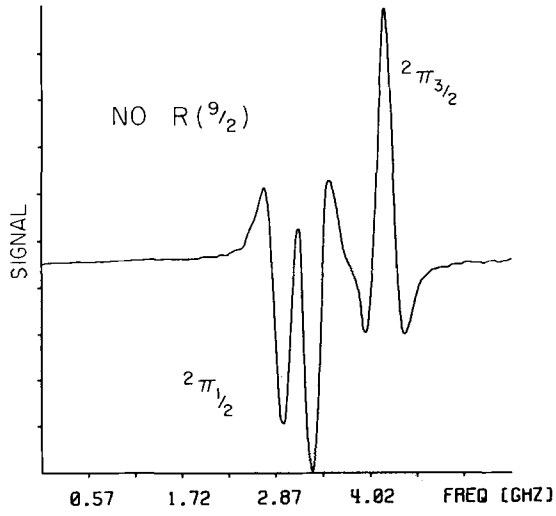

FIG. 4. A typical portion of the NO spectrum in magnetic rotation showing both $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ transitions.

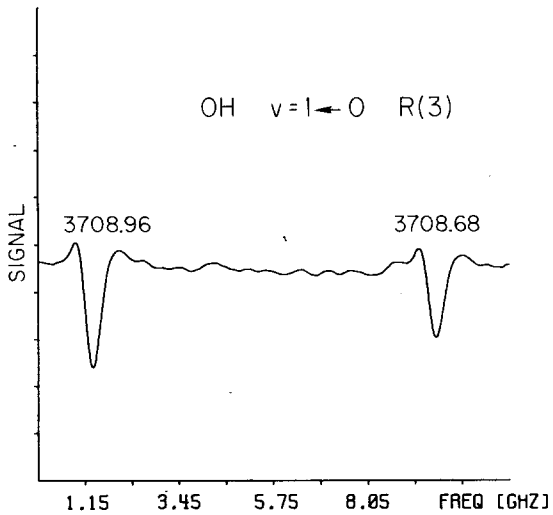

FIG. 5. The two Λ-doubling components of OH $v=1\leftarrow 0$ $R(3)F_1$ observed in the products of a microwave discharge in water. The pathlength is 20 cm.

ponents of this band were recently measured by difference frequency laser spectroscopy.[16] It is thus possible to obtain both relative (by comparison to simple absorption and Zeeman modulation spectroscopy) and absolute measurements of the sensitivity of the magnetic rotation technique.

Figure 3 shows a comparison of the $Q(3/2)^2\Pi_{3/2}$ 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[16] the minimum detectable peak absorption coefficient can be estimated as 10^{-5} cm^{-1}.

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. 4. The splitting of the $^2\Pi_{1/2}$ transition is due to Λ doubling. The $^2\Pi_{3/2}$ R-branch phase is inverted compared 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.

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. 5. 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 spectra study.[17]

ACKNOWLEDGMENTS

This work was supported by National Science Foundation Grant CHE-7826572, Dept. of Energy Contract No. DE-AS05-78ER10477, and Grant C-586 from The Robert A. Welch Foundation.

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