Sensitivity enhancement of laser absorption spectroscopy by magnetic rotation effect

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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. 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), and nearly as high sensitivities have been achieved in mid-infrared LMR. 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 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.

Although active amplitude stabilization schemes 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. The interferometer scheme for saturation spectroscopy with cw dye lasers developed by Kowalski, Hill, and Schawlow 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 Hänisch but is much easier to analyze theoretically, since saturation

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

\textbf{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
\( \Delta \phi = 0 \) (\( Q \) branch). In the presence of a magnetic field
along the direction of propagation, the transition splits
symmetrically into a \( \Delta M = +1 \) and a \( \Delta M = -1 \) com-
ponent with the former absorbing only right hand circularly
polarized light. As a light beam, originally linearly
polarized, propagates through the sample, the polariza-
tion becomes elliptical due to preferential absorption
of one circular component and the axis of polarization
rotates because the two circular components have differ-
ent refractive indices. If a nearly crossed polarizer is
placed in the plane 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 \( \varphi \) 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,
\( \varphi \) 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 recombing the two cir-
cularly polarized components, which will now have dif-
ferent 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
\begin{equation}
P(\varphi) = (P_\theta/2) \exp(-2I_\Delta L) \left( \cos(I_\Delta L) - \cos(R_\Delta L + 2\varphi) \right),
\end{equation}
where \( P(\varphi) \) is the power passed through the polarizer
after the sample which is oriented at an angle \( \varphi + \pi/2 \nwith respect to the incident plane of polarization, \( P_\theta \)
the power incident on the sample, \( I_\Delta \) is the average
attenuation of the fields of the two circular waves, \( L \)
the path length, \( I_\Delta \) is the difference in the attenuation
of the fields of the two circular waves (RHC - LHC),
and \( R_\Delta \) is the difference in the real parts of the field
propagation constants for the two circular polarizations
(again RHC - LHC). For a weak absorption line and
small \( \varphi \) (nearly crossed polarizer), Eq. (1) reduces to
\begin{equation}
P(\varphi) = (P_\theta/2) \left[ 1 - \cos(2\varphi) + R_\Delta \sin(2\varphi) \right]
\end{equation}
neglecting terms in the square of the propagation con-
stants and assuming that the polarizers will not be ex-
actly crossed.

In the absence of the magnetic field \( R_\Delta \) is zero. With
the field on, the \( \Delta M = +1 \) and \( \Delta M = -1 \) components
are separated in frequency by \( 2g\delta H \), and \( R_\Delta \) is the difference
between two terms each of which is given by
\begin{equation}
R_\Delta = (\mu_{j\mu})^2/2aH \varepsilon_j (N_1 - N_2) \Re Z \abs(\Delta \nu_j + i\Delta)/u, \tag{3}
\end{equation}
where \( \mu_{j\mu} \) is the transition dipole moment, \( u = (2\pi T/m)^{1/2} \)
the most probable velocity, \( N_1 \) and \( N_2 \) are the lower
and upper state particle densities of the two levels
(\( \text{cm}^{-3} \)), \( Z \) is the plasma dispersion function, \( \Delta \nu_j \)
the frequency displacement from the peak absorption of the component, \( \Delta \) is the homogenous
linewidth, and \( \lambda \) is the laser wavelength.

The plasma dispersion function is given by
\begin{equation}
Z(\xi) = \pi^{-1/2} \int_{-\infty}^{\infty} dx \exp(-x^2)/(\xi - x), \tag{4}
\end{equation}
where \( \xi \) is complex and \( \Im \xi > 0 \) and arises in this problem
when the homogeneously broadened complex electric
field propagation constants
\begin{equation}
k = \left( \frac{2\pi \nu_c}{c} \right) + \left( \frac{\mu_{j\mu}^2 \nu}{2\hbar c e_0} \right) (N_1 - N_2) \nu -(\nu_0 - \nu_j g\delta H)
\end{equation}
are averaged over the Doppler distribution of \( \nu_0 \)’s
\begin{equation}
f(\nu_0) = \frac{\lambda}{u \sqrt{\pi}} \exp \left( -\left( \frac{\nu_0 - \nu_j g\delta H}{\lambda} \right)^2 \right),
\end{equation}
where \( \nu_j \) is the center frequency of the Doppler
broadened line.

By employing an alternating magnetic field,
\begin{equation}
H = H_0 \sin2\pi ft,
\end{equation}
and thereby modulating the molecular absorption, base-
line drift due to drift in the laser intensity can be elimi-
nated. 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 ex-
pected 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 \( P_T = P_\theta (1 - \cos 2\varphi)/2 \), and therefore
the signal can be written as
\begin{equation}
S = (P_T P_\theta)^{1/2} R_\Delta L.
\end{equation}
Defining the extinction ratio of the polarizer as \( \xi \),
and following the analysis of H"onisch, \textsuperscript{8} the maximum reduc-
tion in source noise is found when the polarizer is
deliberately offset so that the total transmitted light
is \( 2\xi P_\theta \). The signal to transmitted power ratio is given by
\begin{equation}
S/P = R_\Delta L/2(\xi)^{1/2}
\end{equation}
In our experiments the sensitivity is limited by the
polarizer extinction ratio, \( \xi \). 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 \( \xi P_\theta \) is

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FIG. 1. Calculated line shapes for modulated magnetic rotation spectroscopy. Three ratios of homogeneous to Doppler widths are used corresponding to \( x = \frac{\Delta \omega}{\omega} \) 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 \( 1/\omega \) Doppler half-width is 1 GHz.

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,

FIG. 2. Experimental arrangement.

based on a previous design, \(^6\) will be described elsewhere. \(^11\) 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 \( \sim 10^{-5} \). The air-cooled solenoid was usually driven at 216 Hz and 4 A peak current providing a peak field of \( \sim 450 \) G. The pathlength modulated by the solenoid is \( \sim 20 \) 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.

RESULTS

The system was tested by observing the first overtone band of NO at 2.7 \( \mu \). 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. 3. Comparison of the signals for magnetic rotation and simple Zeeman modulation under the same conditions for the \( v'(3/2)^2 \Pi_{3/2} \) line of the \( v = 2 \rightarrow 0 \) of NO.

FIG. 4. A typical portion of the NO spectrum in magnetic rotation showing both \( ^2 \Pi_{3/2} \) and \( ^2 \Pi_{1/2} \) transitions.
enhancement of laser absorption spectroscopy.

components of this band were recently measured by difference frequency laser spectroscopy. 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 $Q(3/2)^3\Pi_{1/2}$ 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 the minimum detectable peak absorption coefficient can be estimated as $10^{-5}$ cm$^{-1}$.

Because of spin un-coupling both $^3\Pi_{1/2}$ and $^3\Pi_{3/2}$ levels can be Zeeman modulated. Such a magnetic rotation spectrum is shown in Fig. 4. The splitting of the $^3\Pi_{3/2}$ transition is due to $\Lambda$ doubling. The $^3\Pi_{3/2} R$-branch phase is inverted compared with the $^3\Pi_{3/2} Q$ 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 $\Lambda$-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.

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