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Observation of Anomalous Zeeman Effect in Infrared Transitions of $^1\Sigma$ CO_2 and N_2O Molecules*

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The Zeeman effect in $^1\Sigma$ CO_2 and N_2O molecules arising from small rotational magnetic moments is observed in several infrared rotation-vibration bands using Doppler-free resonances in gas samples subjected to a magnetic field. Utilizing entire rotation-vibration bands allows measurements of the excited-state molecular g factors and a precise determination of the small dependence [(1–2)%] of the g factors on vibrational states which gives rise to an anomalous Zeeman effect. The signs of the g factors are also determined.

Doppler-free resonances observed in the entire range of transitions of a rotation-vibration band can reveal features not obtainable from the studies of an isolated transition in the band. This Letter reports studies of Doppler-free resonances of the 9- and 10-μm band CO_2 transitions and the 10-μm band N_2O transitions in gas samples subjected to a magnetic field (10 kG). The Zeeman splitting arising from the rotational magnetic moment is observed and studied in detail throughout the entire band. These studies have made possible a precise measurement of the dependence of the molecular g factor on the vibrational quantum number which gives rise to an anomalous Zeeman effect.

The experimental method consists of observing narrow Doppler-free resonances (linewidths ~100 kHz, half width at half-maximum) in a gas sample interacting with the standing-wave field produced by a highly stable, single-frequency laser.[1] The detection of these resonances is achieved by measuring the change in the 4.3-μm fluorescence[2] ($00^\circ1 \rightarrow 00^\circ0$) as the laser frequency is tuned across the line center. This method makes possible the use of a short absorption path length (~10 cm) for the observation of "hot band" (excited vibrational states) transitions which have a small absorption coefficient (3×10^{-7} cm^{-1} mTorr^{-1}).[1] Furthermore, from an experimental standpoint, the ability to use gas samples occupying a small volume is particularly suited to the use of a high-field electromagnet. Observations can be made over hundreds of rotation-vibration transitions in CO_2 and N_2O. This leads to a precise determination of the difference in the g factors between the two levels of the absorbing transition, Δg, as well as the magnitude and sign of the g factor of each vibrational state.

The experimental apparatus for observing $\Delta M = \pm 1$ ($\vec{E} \perp \vec{H}$) transitions is shown schematically in Fig. 1. The highly stable, free-running CO_2 or N_2O laser utilizes a cavity formed by a diffraction grating to select each transition and a curved mirror mounted on a piezoelectric transducer to enable tunability within the Doppler profile of each transition. A detailed description of the laser is given by Kelly.[3] The requirement of a linearly polarized light, for the observation of $\Delta M = \pm 1$ transitions, prohibits the use of a linear-polarizer–quarter-wave-plate feedback isolator.

The fluorescence signal is detected with a liquid-helium–cooled, large-area (20 mm×20 mm), Cu:Ge detector with a cold interference filter also at liquid-helium temperatures. The cold filter passes radiation only between 4 and 5 μm, eliminating the long-wavelength background blackbody radiation. The detector is found to become noisy when placed directly on top of the absorption cell, where it is in a 10 kG field. Hence, the detector is elevated 6 in. above the absorption cell, where the field is 1 kG. At this height the additional noise is eliminated, provided that the biasing cur-

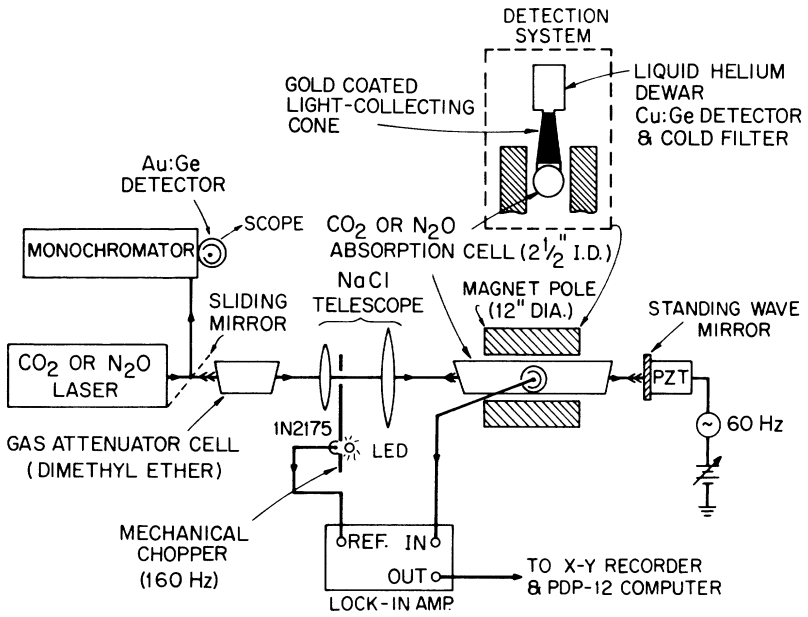

FIG. 1. Experimental apparatus used to observe $\Delta M = \pm 1$ ($\vec{E} \perp \vec{H}$) transitions in CO_2 and N_2O. The telescope and gas attenuator cell are used to obtain a large-diameter (~3 in.) low-intensity beam resulting in narrow linewidths and increased signal to noise. To minimize feedback problems, the position of the standing-wave mirror is modulated by mounting it on a piezoelectric transducer (PZT) driven by a 60-Hz signal. A light-collecting cone is used to elevate the Cu:Ge detector out of the high magnetic field (inset).

rent through the detector crystal is parallel to the magnetic field.

The fluorescence signal was observed by mechanically chopping the incident laser radiation at 160 Hz and synchronously detecting the resultant modulation signal on the fluorescence intensity with a lock-in amplifier (time constant = 0.3 sec). The output of the lock-in amplifier is displayed on an X-Y recorder as the laser frequency is swept across the line center. The lock-in output is also sent into a PDP-12 computer for data analysis and storage.

Before describing the experimental results, let us summarize the expected $\Delta M = \pm 1$ intensity patterns for the various transitions contributing to the line shape. The intensity of each transition is proportional to the fourth power of its electric dipole matrix element, μ (weak saturation). The transition frequencies in the presence of a magnetic field[4] are given by

$$\nu_{\pm}(M_2) = \nu_0 + [(g_2 - g_1)M_2 \pm g_1]\mu_N H/h, \quad (1)$$

where the $\pm$ subscript refers to $\Delta M = \pm 1$ transitions, g_1 and g_2 are the molecular g factors for the upper and lower levels, respectively, M_2 is the lower-level magnetic quantum number, μ_N is the nuclear magneton, H is the magnetic field strength, and h is Planck's constant. Inspection of Eq. (1) shows that a difference between the upper and lower level g factors results in an M-dependent splitting. In the experiment reported here, the linewidth of the individual M transitions is greater than the splitting between adjacent M components $|(g_2 - g_1)\mu_n H/h|$. Thus the $\Delta M = +1$ (or $\Delta M = -1$) transitions appear overlapping and unresolved. Nevertheless, much accurate information on the anomalous Zeeman effect can be obtained by noting that, for high J transitions, where M_2 can take on large values, a small difference in the g factors can produce a dramatic effect on the observed splitting of the unresolved ν_+ components and the unresolved ν_- components.

To further clarify the anomalous feature of the resultant line shape due to the Zeeman effect, a comparison of the intensity patterns for $P(4)$ and $R(4)$ $\Delta M = \pm 1$ transitions is shown in Fig. 2. In this figure, the difference in the g factors is attributed to a pure vibrational effect.[5] The pattern is constructed assuming that $|g_2| > |g_1|$ and $g_i < 0$ ($i = 1, 2$), where 1 and 2 now refer to the upper and lower *vibrational* levels.[6] In this case, the maximum intensity Zeeman peaks are displaced outward for the P branch and inward for the R branch.[7] Increasing the rotational quantum number J of the transitions enhances this effect. If $|g_1| > |g_2|$ instead, the intensity patterns of the P

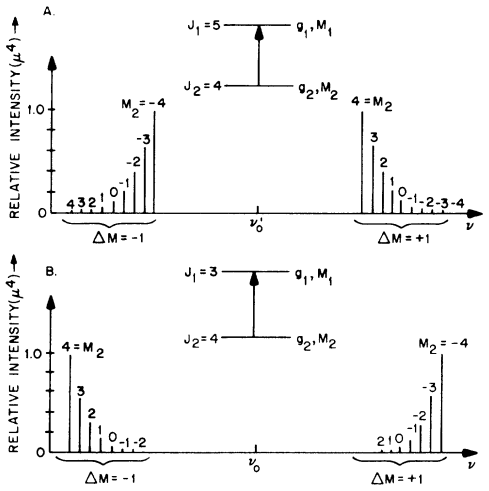

FIG. 2. Anomalous Zeeman effect for $P(4)$ and $R(4)$ transitions. It is assumed that $\Delta g \ll g$. The upper spectrum (a) belongs to the R-branch line and the lower (b) belongs to the P-branch line when the magnitude of the lower-level g factor is larger than that of the upper-level g factor; otherwise, the reverse would be the case. (The crossover resonances appear at ν_0' and ν_0 and are not shown.)

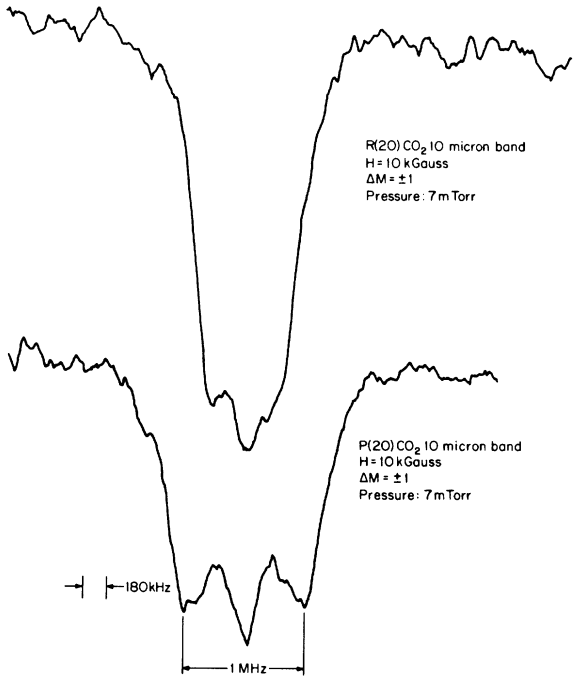

FIG. 3. Typical high-J, $\Delta M = \pm 1$, P- and R-branch anomalous Zeeman spectra. The noise and slight background slope is due to feedback. Note that the individual M transitions within each Zeeman peak are not resolved.

and R branch are interchanged. Consideration of Eq. (1) and $\mu^4(J,M)$ shows that a difference in the g factors arising from a pure rotational effect results in identical intensity patterns for the P- and R- branch spectra.[5]

Figure 3 shows typical $\Delta M = \pm 1$ intensity patterns ($\vec{E} \perp \vec{H}$) obtained for the $R(20)$ and $P(20)$ transitions in CO_2, which should be compared to the theoretical intensity patterns depicted in Figs. 2(a) and 2(b), respectively. The outer peaks are the ν_+ and ν_- Zeeman components described above. The central peak is the crossover resonance arising from the existence of three-level systems with two transitions sharing a common level (i.e., $M \rightarrow M+1$ and $M \rightarrow M-1$) with overlapping Doppler profiles.[8] From the discussion of Fig. 2. and Eq. (1), one immediately concludes that the difference in the g factors, $\Delta g = g_1 - g_2$, is due primarily to a vibrational effect and that $|g_2| > |g_1|$. A detailed computer curve-fitting analysis of $P(J)$ and $R(J)$ line shapes, for various values of J (typically from $J=4$ to $J=34$) over the rotation-vibration band, is used to obtain the precise values of g and Δg given in Table I.

For N_2O, the observed intensity patterns are better resolved because of the larger molecular g factor. It is interesting to note that the intensity patterns for N_2O (for a 10-kG field) are not further complicated by hyperfine structure.[9] For zero magnetic field the hyperfine splitting of the strongest hyperfine components is ~10 kHz or less for transitions with $J \gtrsim 2$ and is not resolvable in this experiment.

In order to measure the sign of the g factor, a small absorption cell was placed in the 3.5-in. gap of the electromagnet. The cell was construct-

TABLE I. Molecular g factors (in nuclear magnetons) for $C^{12}O_2{}^{16}$ and $N_2{}^{14}O^{16}$.

	$\Delta g = g_1 - g_2$	g_1, g_2
CO_2[a] 9.6 μm ($1 \equiv 00°1, 2 \equiv 02°0$)	0.001 00 ± 0.000 06	−0.052 ± 0.003
CO_2[a] 10.6 μm ($1 \equiv 00°1, 2 \equiv 10°0$)	0.001 00 ± 0.000 06	−0.053 ± 0.003
N_2O[b] 10.7 μm ($1 \equiv 00°1, 2 \equiv 10°0$)	0.000 77 ± 0.000 08	−0.077 ± 0.008

[a] $g_{gnd} = (-)0.055\,08 \pm 0.000\,05$ (Ref. 10).
[b] $g_{gnd} = (\pm)0.086 \pm 0.0004$ (Ref. 9).

ed in such a way that right- or left-circularly polarized light in the form of a standing wave could propagate along the magnetic field axis. A CdS quarter-wave plate was used to produce either right- or left-circularly polarized radiation, and the slow axis of the CdS plate was checked using a NaCl Fresnel rhomb. Having determined the sense of the circular polarization, one finds $\Delta M = +1$ transitions shifted up in frequency and $\Delta M = -1$ transitions shifted down in frequency for both CO_2 and N_2O. This corresponds to a negative g factor [see Eq. (1)].

In Table I, we show the ground-state (00°0) molecular g factors measured by Cederberg, Anderson, and Ramsey[10] for CO_2 using a molecular-beam magnetic resonance method and by Jen[9] for N_2O using microwave absorption spectroscopy.

In the case of CO_2, the values of g and Δg for the excited vibrational states of the 9.6- and 10.6-μm rotation-vibration bands are the same within the experimental error. This is not unexpected because the (10°0) and (02°0) levels interact strongly via the Fermi resonance. The primary source of uncertainty in these measurements can be attributed to feedback effects.[11,12] The range assigned to the entries in Table I is a quadratic combination of a standard deviation in the band averaged g or Δg value and a systematic uncertainty arising from the calibration of the laser frequency and of the magnetic field.

Recently, laser spectroscopic techniques have been applied to the measurement of the molecular g factor of $^1\Sigma$ CH_4. Luntz and Brewer[13] using a level-crossing technique and Uzgiris, Hall, and Barger[14] using a Lamb-dip technique observed the Zeeman effect on a single transition in CH_4, which is coincident with the 3.39-μm He-Ne laser. Since only a single transition in the band is available for the observation, an accurate measurement of the anomalous Zeeman effect was not possible.[15]

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[5]For a pure vibrational effect, the g factor is assumed to be a function of vibration only. In this case, the sign of Δg is the same for the P- and R-branch transitions. For a pure rotational effect, the g factor is assumed to be a function of J only. This means that Δg is of opposite sign for the P- and R-branch transitions. In both cases, P- and R-branch matrix elements peak on oppositely signed values of M.

[6]Inspection shows that changing the sign of the g factor does not alter the appearance of the intensity patterns.

[7]In the case of $\Delta M = 0$ ($\vec{E} \parallel \vec{H}$) transitions, one finds that the strongest transition matrix element is split the least, and therefore, the effect of the magnetic field on the nonlinear resonance is slight.

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[11]The N_2O laser is more sensitive to feedback than the CO_2 laser because of its lower gain. This results in a larger error for the N_2O measurements. (See Ref. 3.)

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