Simplification of Spectra by Polarization Labeling*

R. Teets,† R. Feinberg, T. W. Hänsch, and A. L. Schawlow

Department of Physics, Stanford University, Stanford, California 94305

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Polarization labeling is a new method for studying excited states of molecules. Light-induced anisotropy is used to label a molecular ground-state level, and all optical transitions which share this common lower level are detected. Polarization labeled spectra of Na_2 were recorded using pulsed dye lasers. These spectra are easier to interpret than absorption spectra. Collision processes and perturbations of the A state of Na_2 were also observed.

We report on a new technique for unraveling the complexities of molecular spectra. The methods of polarization spectroscopy[1] and lower level labeling[2] are combined to detect all transitions which share a common lower level. The technique produces bright-line spectra which resemble those from laser-excited fluorescence, but which provide direct information about the spectroscopic constants and quantum numbers of the upper state rather than the lower state. This ability to probe the excited states may prove quite useful, since other techniques such as infrared, Raman, and resonance fluorescence spectroscopies are mainly applicable to the study of ground states. In particular, our method can be used to study perturbations of the upper states, transitions from specific ground-state levels to the dissociation edge, variation of the Franck-Condon values, and collision processes.

The experimental setup is shown in Fig. 1. A gas sample is placed between crossed polarizers through which a broadband laser probe beam is directed. The light flux through the crossed polarizers provides a sensitive measure of optical anisotropies in the gas sample. Such anisotropies may be induced by a polarized narrowband laser tuned to a molecular transition. A circularly polarized pump laser produces gyrotropic birefringence and circular dichroism by differentially depleting the various degenerate angular

FIG. 1. Experimental arrangement.

momentum sublevels of the lower state.[3] Similarly, a pump laser that is linearly polarized at 45° to the probe will produce linear dichroism and birefrigence. The induced anisotropy alters the probe polarization at those frequencies which interact with the oriented or aligned molecules. Light at these frequencies, including all transitions which have the same lower level as the pumped transition, can then pass through the crossed polarizers and be analyzed in a spectrograph. Note that with minor experimental changes, the absorption and resonance fluorescence spectra could be recorded on the same plate with the polarization spectra.

The calculation of the signal intensity is similar to that given by Wieman and Hänsch[1] except that here we assume the pump saturates the whole Doppler width of the transition. With perfectly crossed polarizers, and assuming that only selective depletion of the common lower level contributes to the anisotropy, the signal at resonance is given to lowest order by

$$I = I_0 [\tfrac{1}{4}\alpha_0 l (\Delta N/N)\xi]^2.$$

Here I_0 is the probe intensity on resonance, α_0 is the unsaturated probe absorption, l is the cell length, and $\Delta N/N$ is the fractional change in the population of the lower level due to the pump laser. The dimensionless polarization factor ξ represents the relative magnitude of the dichroism for the probe light and plays the same role as the factor $1-d$ in Ref. 1. It depends on the polarization of the pump laser, the angular momentum J of the lower level, and the change of angular momentum for both the pump and probe transitions. In a rate-equation approach[1] this factor can be calculated easily from sums of Clebsch-Gordan coefficients if there is no additional degeneracy. For the large angular momenta associated with molecules the factor has rather simple limiting values. For a circularly polarized pump, $\xi = \tfrac{3}{2}$
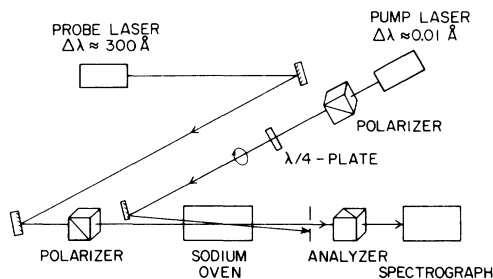
unless one or both of the transitions has $\Delta J = 0$ in which case the value of ξ is decreased by a factor of $1/J$ or $1/J^2$, respectively. For this reason, Q branches ($\Delta J = 0$) cannot usually be detected if the pump is circularly polarized. If the pump laser is linearly polarized at $45°$ to the probe polarizers, on the other hand, $\xi = \frac{3}{10}$ except that if one or both of the transitions has $\Delta J = 0$, the anisotropy is increased by a factor of 2 or 4, respectively.

To test the method, we recorded spectra of molecular sodium in the blue-green band ($B^1\Pi_u \leftarrow X^1\Sigma_g^+$) and in the red band ($A^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$). The sodium was contained in a stainless steel oven with an active region of about 40 cm at a temperature near $300°C$ corresponding to a density of about 5×10^{12} molecules/cm^3. A buffer gas of argon at 0.2 Torr was used to protect the quartz windows. Both lasers were pumped by the same Molectron UV1000 nitrogen laser. The pump laser was of the Wallenstein and Hänsch[4] and Hänsch[5] design, with an intracavity etalon. A single traveling wave amplifier was used, yielding a peak power of several kilowatts in a bandwidth of 1 GHz and a pulse length of about 5 nsec. The broadband probe laser consisted of a dye cell and a single front surface aluminized mirror. The probe peak power was 20 kW with a bandwidth of about 300 Å. The beam diameter in the sodium oven was about 1 mm. Air spaced Glan Thompson prisms were used to polarize and analyze the probe. The quartz oven windows were squeezed gently to reduce birefringence due to internal strain.[1] The spectra were recorded photographically on a 1-m Jarrel-Ash spectrograph in Ebert mount (8.2 Å/mm dispersion and 50-μm entrance slit width). Kodak Royal Pan film (ASA 400) and Polaroid 107 film (ASA 3000) were used, and exposure times from a few seconds to ten minutes were required.

In the first part of the experiment, the pump laser was tuned to a $B \leftarrow X$ transition near 4825 Å and spectra were taken using a blue probe which covered the spectral region around the pump wavelength. This was repeated for several adjacent absorption lines, all within 0.5 Å. Six such spectra are shown in Fig. 2. The spectrum at the bottom of the figure was taken with a linearly polarized pump and hence all three branches appear. For the other five spectra, the pump was circularly polarized, so only the P and R branches appear. For the fourth spectrum, the pumped transition was a Q branch, so the signal intensity was decreased by a factor of $1/J^2$ and
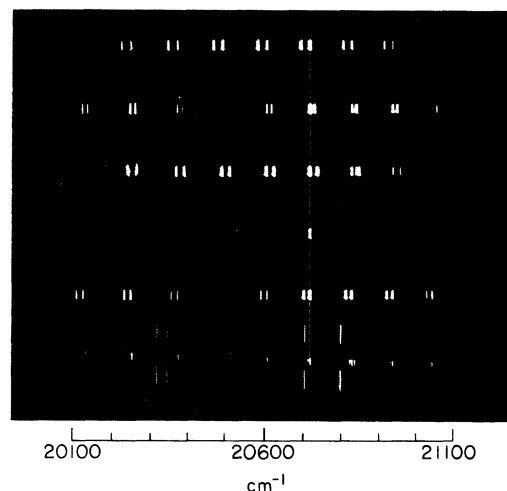

FIG. 2. Polarization labeled spectra of Na$_2$ $B^1\Pi_u$ band. For the top five spectra the pump laser was circularly polarized. For the bottom spectrum the pump was linearly polarized. The dotted line indicates the transition that was pumped. Starting from the top the pumped transitions were $(4,50) \leftarrow (0,49)$, $(5,24) \leftarrow (1,25)$, $(4,41) \leftarrow (0,42)$, $(5,29) \leftarrow (1,29)$, $(5,34) \leftarrow (1,33)$, $(1,25)$, $(4,41) \leftarrow (0,42)$, $(5,29) \leftarrow (1,29)$, $(5,34) \leftarrow (1,33)$, and $(5,29) \leftarrow (1,29)$. The doublets on the left end of each spectrum represent the transition to $v' = 0$.

only the scattered pump light was detected. Since the doublets end abruptly at the low-frequency end, the transition to $v' = 0$ can be recognized and the upper state vibrational quantum numbers can be assigned easily. The assignment of the quantum numbers was verified using the known spectroscopic constants.[6,7] The absence of transitions to $v' = 3$ in some of the spectra is due to the small Franck-Condon factor for ($v' = 3 \leftarrow v'' = 1$) transitions.[7] The spacing between adjacent doublets gives an approximate value of the upper state vibrational constant ω_e. The spacing between components of a doublet can be used to calculate the rotational constant B if the angular momentum J of the state is known. (If, for example, the ground-state constants are known, J can be determined from the fluorescence due to the pumped transition.)

The wavelengths of the series of doublets for seven different pump transitions were determined by measuring the positions of the doublets relative to xenon reference lines using a Grant comparator. The first few Dunham coefficients were determined from a least-squares fit of the data. These agreed to within a few percent with the values of Kusch and Hessel.[6] The utility of this method for determining upper state spectroscopic constants should be apparent.
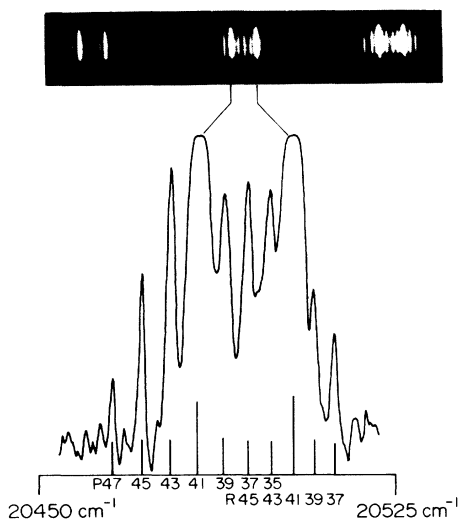
FIG. 3. Spectrum showing collisional transfer of polarization. The circularly polarized pump laser was tuned to the $B(4,40) \leftarrow X(0,41)$ transition. The $v' = 1$, 2, and 3 doublets are shown at the top. The microdensitometer tracing shows the superposition of collisionally induced doublets for the $v' = 2$ transition.

This method may also prove useful for studying collision processes. For the spectrum shown in Fig. 3, a buffer gas of nitrogen at several hundred Torr was introduced into the oven. Collisions changed the angular momentum of the polarized ground state without randomizing the orientation of the molecules, as one might expect for rapidly spinning symmetric tops.[8] Thus the polarization was distributed among the neighboring ground-state levels. The resulting spectrum is a superposition of doublets due to transitions from these neighboring levels. Because sodium is a homonuclear molecule, collisions do not mix states of odd and even J (corresponding to the ortho and para forms in the X state) and hence J must change in units of two.[2] The assignments of the collisional satellites was verified by comparing the measured wavelengths to those calculated from the spectroscopic constants of Kusch and Hessel. From just the spectrum in Fig. 3, it was possible to calculate the angular momentum and the rotational constants B of both the upper and lower state to 10% accuracy.

A useful feature of this spectroscopic technique is the ability to pump a transition in one band and probe some other band. For example, one could pump an infrared transition where the spectroscopic constants are often well known, and probe a transition in the ultraviolet.[2] We probed the red band of sodium while pumping a transi-
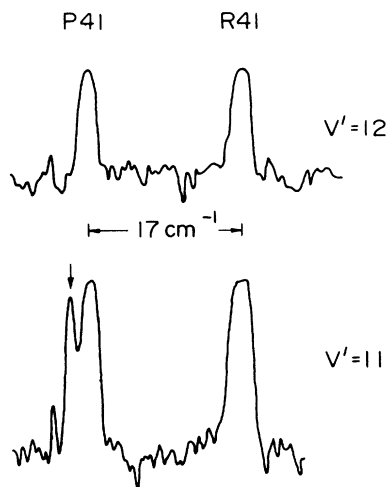

FIG. 4. Two doublets of the $A^1\Sigma_u^+$ state. The arrow points to a weak transition to the $^3\Pi$ level which perturbs the $J' = 40$ component of $v' = 11$. For comparison, the unperturbed $v' = 12$ doublet is also shown.

tion in the blue. Since the transition to $v' = 0$ was not visible, it was not possible in this case to make a simple identification of the upper state vibrational quantum numbers from our spectra. However, even in the absence of such identification, it was possible to determine ω_e and B_e to an accuracy of a few percent from a single spectrum.

It is well known,[6,9] that some levels of the A state are perturbed by nearly coincident levels of a $^3\Pi$ state. An elegant demonstration of this perturbation is shown in Fig. 4. The $(v' = 11, J' = 40)$ level is shifted by the perturbation, so that the doublet splitting is 4% less than the splitting of nearby doublets. Moreover, enough of the character of the singlet state is mixed into the perturbing level to allow a transition to that level of the $^3\Pi$ state. This weak additional line could hardly have been recognized without the simplification provided by lower level labeling. The method could prove useful for investigating other perturbed spectra.

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[1]C. Wieman and T. W. Hänsch, Phys. Rev. Lett. 36, 1170 (1976).
[2]M. E. Kaminsky, R. T. Hawkins, F. V. Kowalski,

and A. L. Schawlow, Phys. Rev. Lett. 36, 671 (1976).

[3]E. Drullinger and R. N. Zare, J. Chem. Phys. 51, 5532 (1969).

[4]R. Wallenstein and T. W. Hänsch, Opt. Commun. 14, 353 (1975).

[5]T. W. Hänsch, Appl. Opt. 11, 895 (1972).

[6]P. Kusch and M. M. Hessel, J. Chem. Phys. 63, 4087 (1975); M. M. Hessel, private communication.

[7]W. Demtröder, M. McClintock, and R. N. Zare, J. Chem. Phys. 51, 5495 (1969).

[8]R. E. Drullinger and R. N. Zare, J. Chem. Phys. 59, 4225 (1973).

[9]W. R. Frederickson and C. R. Stannard, Phys. Rev. 44, 632 (1933).

Observation of Anomalous Zeeman Effect in Infrared Transitions of $^1\Sigma$ CO$_2$ and N$_2$O Molecules*

M. J. Kelly, J. E. Thomas,† J.-P. Monchalin, N. A. Kurnit,‡ and A. Javan

Physics Department, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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The Zeeman effect in $^1\Sigma$ CO$_2$ and N$_2$O 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$_2$O 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°1 → 00°0) 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$_2$O. 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$_2$O 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-
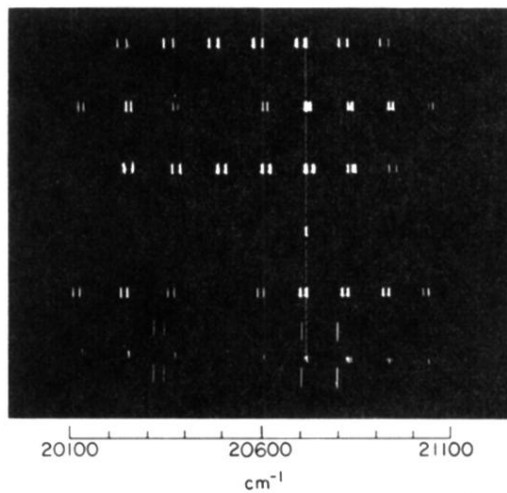
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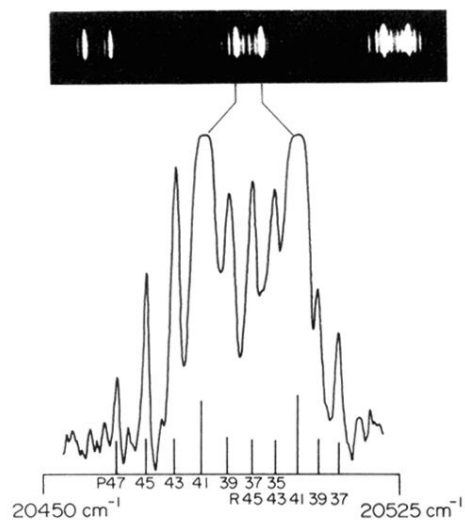spectrum represent the transition to $v' = 0$.

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