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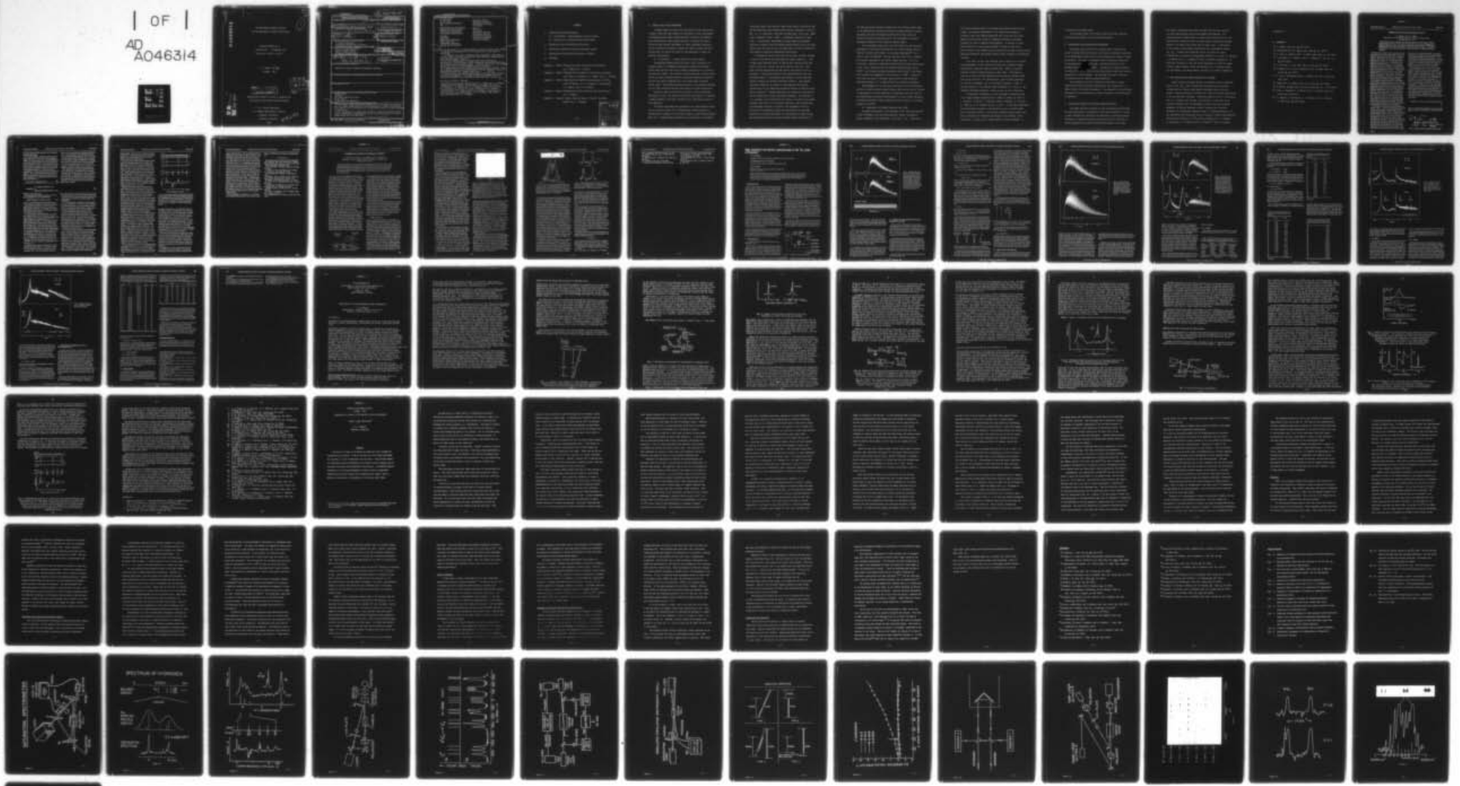

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Ultranarrowband Tunable Dye Laser
for New Approaches to Atomic Spectroscopy

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report summarizes recent progress in the development and improvement of tunable laser systems for novel approaches to atomic and molecular spectroscopy, and in particular for new precision studies of atomic hydrogen.
It reports on:
(a) The development of a highly monochromatic, powerful tunable dye laser system, combining a single-frequency cw dye laser oscillator with a multistage pulsed dye laser amplifier. → over

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No.19 Nitrogen Laser
Ar Ion Laser
Kr Ion Laser
Sum Frequency Generation
ADP

High Resolution Spectroscopy
Doppler-Free Spectroscopy
Two-Photon Spectroscopy
Polarization Spectroscopy

Hydrogen
Lamb Shift
Balmer Beta Transition
Stark Splitting
Fundamental Constants
Quantum Electrodynamics

Molecular Sodium
Absorption Spectrum
Polarization Labeling
Collisions

Benzene
$^1B_{2u}$ State
Two-Photon Spectrum
Rotational Contours
Rotational Constants
Structural Parameters
Coriolis Constants

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No.20 (b) The generation of cw single-frequency coherent radiation near 2430Å by summing the frequencies of a Kr ion laser and a cw dye laser in cooled ADP.

In addition, the report summarizes three experiment, exploring new coherent light techniques for sensitive high resolution spectroscopy of atoms and molecules. These are

(c) The first demonstration of Doppler-free laser polarization spectroscopy, a new technique, which can greatly exceed the sensitivity of saturated absorption spectroscopy. The Stark splitting of the hydrogen Balmer beta line in a glow discharge has been resolved.

(d) A demonstration of polarization labeling of molecular sodium. This new technique simplifies the unraveling of complex absorption spectra by identifying lines with a common lower state.

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(e) High resolution two-photon spectroscopy of the $^1B_{2u}$ state of normal and deuterated benzene. The observed rotational contours have been reported by computer fits, yielding accurate molecular constants.

The report contains 5 reprints:

"Doppler-Free Polarization Spectroscopy" by C. Wieman and T. W. Hänsch, "Simplification of Spectra by Polarization Labeling" by R. Teets, R. Feinberg, T. W. Hänsch, and A. L. Schawlow, "High Resolution Two-Photon Spectroscopy in the $^1B_{2u}$ State of Benzene" by J. Lombardi, R. Wallenstein, T. W. Hänsch, and D. M. Friedrich, "Applications of High Resolution Laser Spectroscopy" by T. W. Hänsch, and "Lasers, Light and Matter" by A. L. Schawlow.

CONTENTS

A. TUNABLE LASER SYSTEM DEVELOPMENT

Although tunable dye lasers for high resolution spectroscopy have reached a relatively high standard of performance, further improvements in wavelength range, power, monochromaticity and spatial and temporal beam characteristics remain highly desirable. Motivated by several envisioned spectroscopic experiments of rather fundamental importance, we have continued our efforts to develop and improve tunable dye laser systems which can provide the tools for new approaches to atomic and molecular spectroscopy.

A1. CW Oscillator - Pulsed Amplifier Dye laser System.

Nitrogen-laser-pumped pulsed dye lasers, built according to our original design,[1] are meanwhile commerically available from several manufacturers and have been used in numerous laboratories for innovative spectroscopic studies. More recently, we have developed a pressure-tuned pulsed dye laser oscillator-amplifier system with dramatically improved spectral and spatial brightness and a very large linear continuous tuning range.[2] This system has already proven to be an extremely powerful tool for high resolution nonlinear spectroscopy of atoms and molecules.

During the report period we have achieved a further substantial improvement in power, and spectral and spatial beam quality, by combining a single-frequency cw dye laser oscillator with a multistage pulsed dye laser amplifier.

The initial experiments were performed with a Spectra-Physics model 375 jet stream dye laser, with 7-diethyl-amino 4-methyl-coumarin in ethylene glycol, pumped by an ultraviolet argon ion laser (Spectra-Physics model 171). Single-frequency operation was achieved with an air-spaced intracavity etalon (free spectral range 30 GHz, mirror reflectivity 30%) and two additional fixed uncoated quartz etalons (thickness 0.1 and 0.5 mm). At 1 W pump power, this laser provides about 10 mW near 4860Å with a linewidth of about 20 MHz , continuously tunable over about 4 GHz . (A substantial improvement in tuning range and wavelength stability is expected from the Coherent Radiation model 599 cw dye laser, which we have been able to order with ONR funds, but whose delivery has been delayed by unexpected engineering difficulties.)

By sending the output of our blue cw dye laser oscillator through a chain of three pulsed dye laser amplifier stages, pumped by a 1 MW nitrogen laser (Molectron model UV 1000) we have achieved output peak powers of more than 100 kW with input powers of less than 1 mW , while virtually maintaining the high spatial beam quality of the cw oscillator. Construction details of the pulsed amplifiers have been described earlier.[2] The amplified beam exhibits a Fourier-transform limited linewidth and excellent amplitude stability. This approach completely eliminates the problem of large spectral fluctuations, characteristic for the amplified spontaneous emission of high gain pulse laser oscillators.[3] Although admittedly more complicated and expensive, the new scheme offers several additional advantages: The frequency of a cw oscillator can be locked much more easily to an atomic or molecular resonance line, which is of particular importance, where extreme long-term wavelength stability is required. The wavelength of such an oscillator can be measured quickly and conveniently with very high precision by counting large numbers of interferometric fringes, as has been demonstrated with two recently developed digital wave meters.[4,5]

The improved spatial coherence together with the increased output power of the amplified beam facilitate nonlinear frequency mixing in crystals and gases, and open interesting new prospects for high resolution vacuum ultraviolet spectroscopy and for the development of accurate wavelength standards in this important spectral region.

We are presently using such a dye laser system in a new precision measurement of the ground state Lamb shift of atomic hydrogen, which is expected to improve the accuracy of our earlier experiments[6,7] by at least an order of magnitude. The new Lamb shift value will be obtained by precisely comparing the two optical energy intervals 1S-2S and 2S,p-4S,P,D observed by simultaneous Doppler-free two-photon spectroscopy of the 1S-2S transition with the frequency doubled pulsed laser at 2430Å [7] and by high resolution polarization spectroscopy[8] of the Balmer beta line with the fundamental cw laser output at 4860Å. Details of this effort are given in the paper "Applications of High Resolution Laser Spectroscopy" by T. W. Hänsch,[9] which is included as Appendix D.

The development of our new laser system has put us in an excellent position to explore several related schemes, which are not only of interest to spectroscopy, but which should be of considerable practical value for such applications as selective photochemistry or laser isotope separation. A detailed discussion of these possibilities will be given in our renewal proposal for 1977/78.

A2. Generation of CW Tunable Radiation near 2430Å.

Two-photon spectroscopy of the hydrogen 1S-2S transition presents a great challenge to the laser spectroscopist, because the expected natural linewidth of this transition is only about 1 Hz , much below the Fourier-transform limit of a nitrogen-laser-pumped pulsed dye laser system. Any precision measurement of the transition wavelength or frequency, which even remotely approaches this resolution, will yield important new precision values of fundamental constants and provide stringent new tests of quantum electrodynamics. In addition it would open prospects for a new primary standard of length or time, which would be based on this simples atom, and would thus provide an intellectually appealing transparent relationship between primary standards and fundamental constants.

In an effort to meet this challenge, and in parallel to our pulsed laser development, we have exlored the possibility to generate highly monochromatic continuous tunable radiation near 2430Å by nonlinear frequency mixing of single-frequency cw laser light. Unfortunately, there is at present no known nonlinear optical material available which would permit efficient 90° -phase-matched second harmonic generation at this short wavelength. But it is possible to generate 2430Å as the sum frequency of two different laser wavelength is a crystal of ADP (ammonium dihydrogen phosphate), cooled to near its Curie temperature.

In preliminary experiments, we have succeeded in generating about .1 mW single-frequency radiation near 2430Å by summing the output of a 500 mW Kr ion laser at 4131Å and a 200 mW rhodamine 6G dye laser at 5901Å in a 5 cm long ADP crystal at 160 K . Considerably improvement in power should be possible if the nonlinear crystal is placed inside one or both laser cavities. But even the presently achieved power levels may be sufficient for two-photon spectroscopy of the hydrogen 1S-2S transition, if the gas cell is placed inside a confocal resonator, to recirculate the available light.

The described scheme is of obvious interest for high resolution ultraviolet spectroscopy of other atoms and molecules.

B. DOPPLER-FREE LASER POLARIZATION SPECTROSCOPY

During the report period we have demonstrated a sensitive new method of Doppler-free spectroscopy, monitoring the nonlinear interaction of two monochromatic laser beams in an absorbing gas via changes in light polarization. The signal to background ratio can greatly surpass that of saturated absorption spectroscopy. Polarization spectra of the hydrogen Balmer β line at 4860Å, recorded with a single-frequency cw coumarin dye laser, reveal the Stark splitting of single fine structure components in a Wood discharge. The experiment indicates interesting new possibilities for sensitive plasma diagnostics.

The principles of the new technique are described in a paper "Doppler-Free Laser Polarization Spectroscopy" by C. Wieman and T. W. Hänsch,[8] which is included as Appendix A. The prospects for new precision experiments in atomic hydrogen are further discussed in the review paper[9] in Appendix D.

D. POLARIZATION LABELING OF MOLECULAR ABSORPTION SPECTRA

The highly sensitive technique of laser polarization spectroscopy[8] has also been applied to the method of lower level labeling,[9] to provide a useful technique for unraveling the complexities of molecular spectra. Molecules in a selected rovibronic ground state level are oriented by optical pumping with circularly polarized monochromatic laser light.

All optical transitions which share the same lower level are detected via their light-induced optical birefringence and dichroism. The resulting spectra resemble those of laser-excited fluorescence, but they provide direct information about the spectroscopic constants and quantum numbers of the upper state rather than the lower state. A description of this method of polarization labeling and first experimental results for Na_2, obtained with pulsed dye lasers, are given in a paper "Simplification of Spectra by Polarization Labeling" by R. Teets, R. Feinberg, T. W. Hänsch, and A. L. Schawlow,[10] which is included as Appendix B. An additional discussion of this and related experiments is found in a paper "Lasers, Light and Matter" which was presented by A. L. Schawlow during his 1976 Frederic Ives Medal Address, and which is included as Appendix E.

D. HIGH RESOLUTION TWO-PHOTON SPECTROSCOPY OF BENZENE

Highly resolved rotational spectra of two-photon excited vibrational levels in the $^1B_{2u}$ state of normal and deuterated benzene have been recorded with our pressure tuned powerful narrowband pulsed dye laser system. Different contours are observed for linear and circular polarization of the exciting laser radiation. Theoretical spectra fitted in collaboration with J. R. Lombardi (City College, City University of New York) are in excellent agreement with the experimental results and provide molecular parameters (rotational constants, Coriolis constants and structural parameters) of considerably improved accuracy. A detailed description of the experimental and theoretical results is given in a paper "High Resolution Two-Photon Spectroscopy in the $^1B_{2u}$ State of Benzene" by J. R. Lombardi, R. Wallenstein, T. W. Hänsch, and D. M. Friedrich,[11] which is included as Appendix C.

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APPENDIX A.

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Doppler-Free Laser Polarization Spectroscopy*

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(Received 25 March 1976)

We have demonstrated a sensitive new method of Doppler-free spectroscopy, monitoring the nonlinear interaction of two monochromatic laser beams in an absorbing gas via changes in light polarization. The signal-to-background ratio can greatly surpass that of saturated absorption. Polarization spectra of the hydrogen Balmer-β line, recorded with a cw dye laser, reveal the Stark splitting of single fine-structure components in a Wood discharge.

We report on a sensitive new technique of high-resolution laser spectroscopy based on light-induced birefringence and dichroism of an absorbing gas. Polarization spectroscopy is related to saturated-absorption[1] or saturated-dispersion[2] spectroscopy, but offers a considerably better signal-to-background ratio. It is of particular interest for studies of optically thin samples or weak lines and permits measurements even with weak or fluctuating laser sources. We have studied the Balmer-β line of atomic H and D near 4860 Å by the new method, using a *single-frequency* cw dye laser. The spectra reveal for the first time the Stark splitting in the weak axial electric field of a Wood-type gas discharge.

For saturation spectroscopy it is well known that the signal magnitude depends on the relative polarization of saturating beam and probe.[3,4] The possibility and advantage of using the resulting optical anisotropy in a sensitive polarization detection scheme seem to have gone unexplored, however. On the other hand, the phenomena of light-induced birefringence and dichroism are quite common in optical-pumping experiments with incoherent light sources.[5] Recent related experiments[6,7] encourage us to expect that high-resolution polarization spectroscopy will also prove useful for studies of two-photon absorption and stimulated Raman scattering in gases.

The scheme of a polarization spectrometer is shown in Fig. 1. A linearly polarized probe beam from a monochromatic tunable laser is sent through a gas sample, which is shielded from external magnetic fields to avoid Faraday rotation. Only a small fraction of this beam reaches a photodetector after passing through a nearly crossed linear polarizer. Any optical anisotropy which changes the probe polarization will alter the light flux through the polarizer and can be detected with high sensitivity. Such an anisotropy can be induced by sending a second, circularly polarized, laser beam in nearly the opposite direction through the sample. In the simplest case both beams have the same frequency ω and are generated by the same laser. As in conventional saturation spectroscopy, a resonant probe signal is expected only near the center of a Doppler-broadened absorption line where both beams are interacting with the same atoms, those with essentially zero axial velocity.

For a quantitative description we can decompose the probe into two circularly polarized beams, rotating in the same (+) and in the opposite (−) sense as the polarizing beam. As long as the probe is weak these two components can be considered separately. The polarizing beam in general induces different saturation, i.e., changes in absorption coefficient, $\Delta\alpha^+$ and $\Delta\alpha^-$, and in refractive index, Δn^+ and Δn^-, for these components. A difference $\Delta\alpha^+ - \Delta\alpha^-$ describes a circular dichroism which will make the probe light elliptically polarized, and a difference $\Delta n^+ - \Delta n^-$ describes a gyrotropic birefringence which will rotate the axis of polarization. As long as these polarization changes are small, the complex field amplitude behind the blocking polarizer is given by

$$E = E_0[\theta + (\omega/c)(\Delta n^+ - \Delta n^-)l/2 - i(\Delta\alpha^+ - \Delta\alpha^-)l/4], \tag{1}$$

where E_0 is the probe amplitude, θ is some small angle by which the polarizer is rotated from the

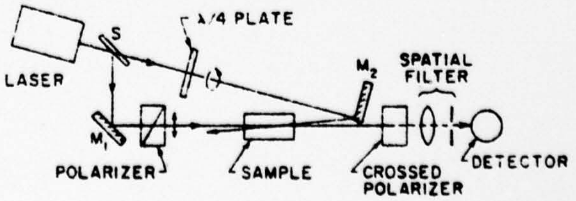

FIG. 1. Scheme of laser polarization spectrometer.

perfectly perpendicular position, and l is the absorption path length.

For low intensities, within third-order perturbation theory[8] and in the limit of large Doppler widths, the interaction of two counterpropagating circularly polarized beams with two levels of angular momentum J and J' can be described simply in terms of a velocity-selective hole burning[1] for the different degenerate sublevels of orientational quantum number m, where the axis of quantization is chosen along the direction of propagation. As in conventional saturation spectroscopy[1] the absorption change as a function of the laser frequency is a Lorentzian function with the natural linewidth γ_{ab}:

$$\Delta\alpha^{+} = \Delta\alpha^{-}/d = -\tfrac{1}{2}\alpha_0 I/I_{sat}(1+x^2). \tag{2}$$

Here, α_0 is the unsaturated background absorption, I is the intensity of the polarizing beam, I_{sat} is the saturation parameter, and $x=(\omega-\omega_{ab})/\gamma_{ab}$ describes the laser detuning from resonance. The absorption change corresponds to the imaginary part of a complex third-order susceptibility, whose real part results in a concomitant change in refractive index, $\Delta n^{\pm} = -\tfrac{1}{2}\Delta\alpha^{\pm}xc/\omega$, in agreement with the Kramers-Kronig relation.

The magnitude of the anisotropy is described by the parameter d and depends on the angular momenta and the decay rates γ_J and $\gamma_{J'}$ of the involved states. If spontaneous re-emission into the lower state is ignored, the steady-state signal contributions of the different orientational sublevels can be added with the help of simple sum rules[4] to yield

$$d \equiv \Delta\alpha^{-}/\Delta\alpha^{+} = \begin{cases} 1-5/(4J^2+4J+2) \text{ for } J=J', \\ (2J^2+5rJ+3)/(12J^2-2) \text{ for } J=J'+1, \end{cases} \tag{3}$$

where $r=(\gamma_J-\gamma_{J'})/(\gamma_J+\gamma_{J'})$.

By inserting these results into Eq. (1), we obtain the light flux at the probe detector

$$I = I_0[\theta^2 + \theta\tfrac{1}{2}sx/(1+x^2) + (\tfrac{1}{4}s)^2/(1+x^2)], \tag{4}$$

where I_0 is the unattenuated probe power and $s = -\tfrac{1}{2}(1-d)\alpha_0 lI/I_{sat}$ gives the maximum relative intensity difference between the two counter-rotating probe components. In practice we have to add an amount $I_0\xi$ to account for the finite extinction ratio ξ of the polarizer.

For a perfectly crossed polarizer, i.e., $\theta=0$, the combined effects of dichroism and birefringence lead to a Lorentzian resonance signal. The signal magnitude is proportional to s^2, i.e., it drops rapidly for small s. Small signals can be detected with higher sensitivity at some small bias rotation $\theta \gg s$. The last term in Eq. (4) can then be neglected and the birefringent polarization rotation produces a dispersion-shaped signal on a constant background. If, as in many practical situations, laser intensity fluctuations are the primary source of noise, a figure of merit for the sensitivity is the signal-to-background ratio. Compared to saturated-absorption spectroscopy, this ratio is improved by a factor $(1-d)\theta/4(\theta^2+\xi)$ which reaches its maximum $(1-d)/8\sqrt{\xi}$ for $\theta=\sqrt{\xi}$.

In addition to the improved sensitivity, such a dispersion-shaped signal is of obvious interest for the locking of the laser frequency to some resonance line. It is also noteworthy that its first derivative has a linewidth smaller than half the natural width, which can greatly facilitate the spectroscopic resolution of closely spaced line components.

For the alternative scheme of a linearly polarized saturating beam, rotated 45° with respect to the probe polarization, it can be shown in analogous fashion that the signal always remains Lorentzian, independent of the polarizer angle θ.

As in saturated-absorption spectroscopy, crossover signals are expected halfway in between two resonance lines which share a common upper or lower level. A third-order nonlinear susceptibility tensor, applicable to this situation, has actually been calculated previously.[3] It predicts that the ratio $\Delta\alpha^{-}/\Delta\alpha^{+}=d$ for certain angular momentum states can exceed 1, unlike the expression (3), and hence give rise to signals with inverted polarization rotation.

For the experimental study of the hydrogen Balmer-β line we used a cw jet-stream dye laser (Spectra-Physics Model No. 375) with 7-diethylamino-4-methyl-coumarin in ethylene glycol, pumped by an uv argon laser (Spectra-Physics Model No. 171). Single-frequency operation was achieved with an air-spaced intracavity etalon (free spectral range 30 GHz; mirror reflectivity 30%) and two additional fixed uncoated quartz etalons (thicknesses 0.1 and 0.5 mm). At 1 W pump power, the laser provides single-mode output of about 10 mW near 4860 Å with a linewidth of about 20 MHz. The laser can be scanned continuously over ~4 GHz by applying linear ramp voltages to the piezotransducers of the cavity end mirror and the air-spaced etalon.

As in the previous saturated-absorption experiment,[9] the hydrogen atoms were excited to the absorbing $n=2$ state in a Wood-type discharge tube (1 m long, 8 mm in diameter, 0.2 Torr, 3 mA dc current). The laser light is sent through a 40-cm-long center section of the positive column. Probe and polarizing beam are each about 1 mm in diameter and have powers of 0.1 and 1 mW, respectively. A mica sheet serves as a $\lambda/4$ retarder for the polarizing beam. To avoid residual Doppler broadening due to a finite crossing angle we operated with collinear beams, replacing mirror M_2 in Fig. 1 with an 80% beam splitter which transmits part of the probe.

Standard Glan-Thompson prism polarizers (Karl Lambrecht) were employed for the probe beam. Birefringence in the quartz windows of the gas cell due to internal strain was reduced by squeezing the windows gently with adjustable clamps. We achieve extinction ratios of 10^{-7} or better in this way, and the possible improvement over saturated-absorption spectroscopy in signal-to-background ratio is on the order of 100–1000. The probe light which passes the blocking polarizer is sent through a spatial filter to eliminate incoherent light emitted by the gas discharge and scattered light from the polarizing beam. Its intensity is monitored with a photomultiplier.

Figure 2 shows a portion of the Balmer-β spectrum plotted versus time during a laser scan of about 5 min duration. To record the derivative of dispersion-shaped resonances, the dye laser was frequency modulated by adding a small audio-frequency voltage to the cavity-mirror tuning ramp, and the resulting signal modulation was detected with a phase-sensitive amplifier. The three strongest theoretical fine-structure transitions in this region are shown on top for comparison. Hyperfine splitting is ignored. The positions of possible crossover lines due to a common upper or lower level are indicated by arrows. Obviously, the polarization spectrum reveals many more components. These have to be ascribed to the Stark splitting in the axial electric field of the positive discharge column.

We have calculated the theoretical Stark pattern for an axial field of 10 V/cm by diagonalizing the Hamiltonian.[10] The positions of the strongest Stark components and their respective crossover lines are indicated in Fig. 2 and agree well with the observed spectrum. The splitting of the upper $4P,D_{3/2}$ level is essentially a linear function of the electric field, and its magnitude can easily be determined to within a few percent from the observed spectrum. The theoretically expected line strengths and the signs of the crossover lines are also in satisfactory agreement with the experiment. The polarization spectrum of light hydrogen looks almost identical to that of deuterium and shows no indication for the 170-MHz hyperfine splitting of the 2S state; the components originating in the $F=0$ state are missing, because atoms in this level cannot be oriented.

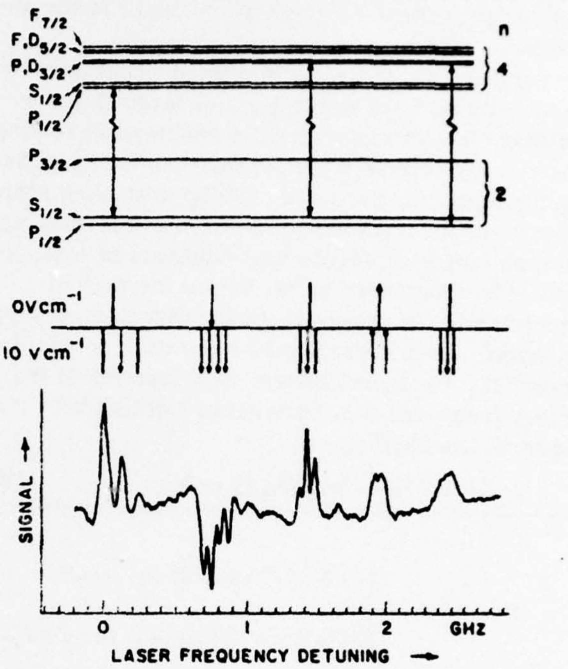

FIG. 2. Polarization spectrum of a portion of the deuterium Balmer-β line. The three strongest fine-structure components and the positions of the strongest Stark components for an axial electric field of 10 V/cm are shown on top for comparison. Crossover lines due to a common upper (↑) or lower (↓) level are indicated by arrows.

The observed Stark pattern changes quite drastically if the laser beams are displaced from the tube axis, indicating the presence of additional radial electric fields due to space and surface charges of cylindrical symmetry. Polarization spectroscopy of the hydrogen Balmer lines thus opens new possibilities for sensitive plasma diagnostics.

The spectrum in Fig. 2 also clearly reveals the different natural linewidths of components originating in the short-living 2P state and the longer-living 2*S* state. The narrowest observed components have a width of about 40 MHz, corresponding to a resolution of about 6 parts in 10^8, i.e., they exhibit more than an order of magnitude improvement over our earlier pulsed-laser saturation spectra.[9] A substantial improvement in the accuracy of the 1*S* Lamb shift is expected, if such a polarization spectrum is used as a reference for the 1*S*-2*S* two-photon spectrum.[9] A still further improvement in resolution should be possible if the laser linewidth is reduced by frequency stabilization. At low electric fields the natural linewidth of the quasi-forbidden 2*S*-4*S* transition is only about 1 MHz. A measurement of the H-D isotope shift to better than 0.1 MHz would confirm or improve the important ratio of electron mass to proton mass, and an absolute wavelength or frequency measurement to better than 6 MHz would yield a new improved value for the Rydberg constant. We are presently exploring these and other possibilities for new precision measurements.

We are indebted to Professor A. L. Schawlow for his stimulating interest in this work, and we thank J. Eckstein for his help in calculating Eq. (3).

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†Hertz Foundation Predoctoral Fellow.

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APPENDIX B.

VOLUME 37, NUMBER 11 PHYSICAL REVIEW LETTERS 13 SEPTEMBER 1976

Simplification of Spectra by Polarization Labeling*

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(Received 16 July 1976)

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 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.

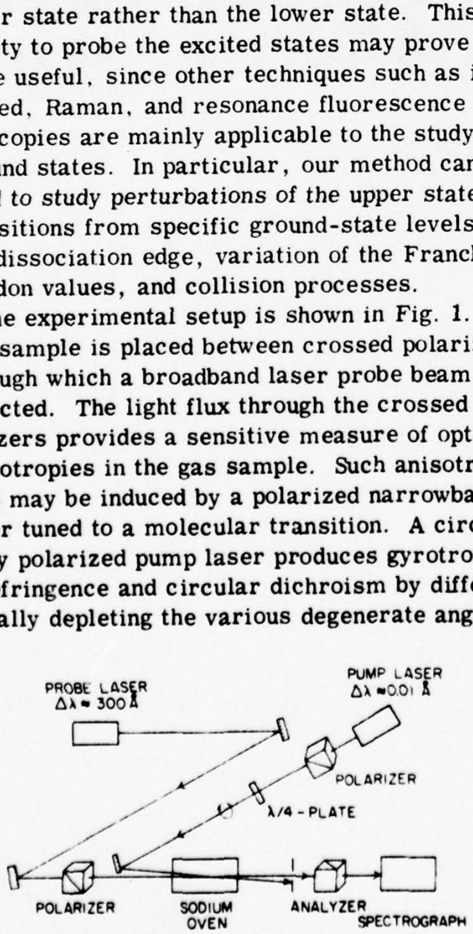

FIG. 1. Experimental arrangement.

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, $\xi = \frac{3}{2}$

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 ($B^1\Pi_u - X^1\Sigma_g^+$) and in the red band ($A^1\Sigma_u^+ - X^1\Sigma_g^+$). 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 $B - X$ 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 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.)

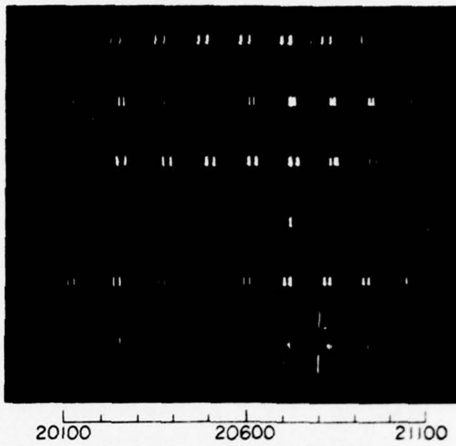

FIG. 2. Polarization labeled spectra of Na_2 $B^1\Pi_u$ band. For the top five spectra the pump laser was circularly polarized. For the bottom spectrum the pump was linearly polarized. The dotted line indicates the transition that was pumped. Starting from the top the pumped transitions were $(4,50)\leftarrow(0,49)$, $(5,24)\leftarrow(1,25)$, $(4,41)\leftarrow(0,42)$, $(5,29)\leftarrow(1,29)$, $(5,34)\leftarrow(1,33)$, $(1,25)$, $(4,41)\leftarrow(0,42)$, $(5,29)\leftarrow(1,29)$, $(5,34)\leftarrow(1,33)$, and $(5,29)\leftarrow(1,29)$. The doublets on the left end of each spectrum represent the transition to $v' = 0$.

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.

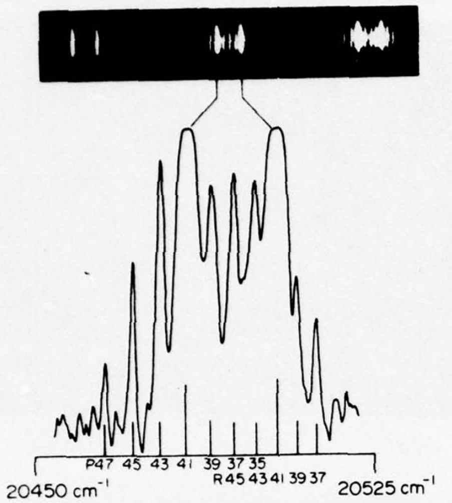

FIG. 3. Spectrum showing collisional transfer of polarization. The circularly polarized pump laser was tuned to the $B(4,40) \leftarrow X(0,41)$ transition. The $v'=1$, 2, and 3 doublets are shown at the top. The microdensitometer tracing shows the superposition of collisionally induced doublets for the $v'=2$ transition.

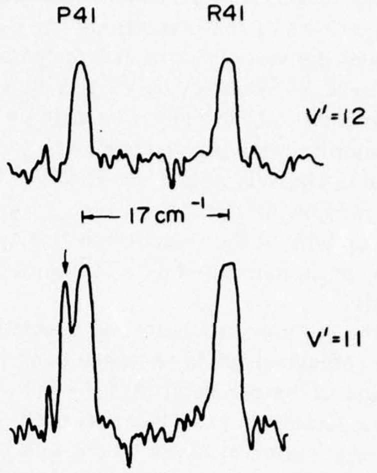

FIG. 4. Two doublets of the $A\,^1\Sigma_u^+$ state. The arrow points to a weak transition to the $^3\Pi$ level which perturbs the $J'=40$ component of $v'=11$. For comparison, the unperturbed $v'=12$ doublet is also shown.

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 transition 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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†National Science Foundation Predoctoral Fellow.

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APPENDIX C.

High resolution two-photon spectroscopy in the $^1B_{2u}$ state of benzene[*]

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Highly resolved rotational spectra of two-photon excited vibrational levels in the $^1B_{2u}$ state of C_6H_6 and C_6D_6 are recorded for linear and circular polarization of the exciting laser radiation, generated with a powerful narrow-band dye laser system. The fitted theoretical spectra are in excellent agreement with the experimental results and provide molecular parameters (rotational constants, Coriolis constants, and structural parameters) of considerably improved accuracy.

I. INTRODUCTION

Since the first observation of two-photon excitation in benzene vapor by Hochstrasser *et al.*[1] several groups have studied the vibronic two-photon transitions from the $^1A_{1g}$ ground state to the $^1B_{2u}$ excited state.[2–4] In these experiments vibrational levels were excited by intense radiation from nitrogen laser pumped tunable dye lasers. The results reported so far provide a good survey of the two-photon spectrum and allowed the assignment of numerous bands. In addition, lifetimes of excited states[6] and the influence of the polarization of the exciting photons on rotational contours have been investigated.[4,5] But due to the rather large bandwidth (1–4 cm^{-1}) of the dye lasers used in these experiments, the spectral resolution was not sufficient for any detailed rotational analysis.

With the development of a narrowband, easily tunable powerful dye laser system[7] (bandwidth < 0.03 cm^{-1}) we could resolve successfully the rotational structure of two-photon as well as one-photon excited bands.[7] Using this laser system we report on the recording of highly resolved spectra of several two-photon excited states in C_6H_6 and C_6D_6. Calculated spectra, fitted to the observed band structures are in excellent agreement with the experimental results.

This first detailed analysis of the rotational spectrum of vibronic two-photon transitions[8] not only confirms previous assignments but also provides rotational constants which are more accurate than those previously obtained from one-photon uv absorption spectra.[9]

II. EXPERIMENTAL

A simplified scheme of the experimental set up is displayed in Fig. 1.

The dye laser, a pressure tuned oscillator amplifier system,[7] generates tunable radiation of narrow linewidth (less than 0.03 cm^{-1}) and high peak power (20–30 kW at 500–520 nm, using a solution of 2×10^{-2} moles/1 Pilot 495 (NEN) in dioxane). The laser radiation linearly polarized by an intracavity and an external polarizing prism is sent through a fresnel rhomb. Depending on the orientation of the polarizing prisms the light leaving the fresnel rhomb is either linearly or circularly polarized. It is focused by a lens of 200 mm focal length to a waist size of 90 μm into a quartz cell containing benzene vapor of about 20 Torr (0 °C). The two-photon excited fluorescence is monitored with a photomultiplier EMI 6256S. Scattered laser light is cut off by three Corning filters 7–54.

Part of the dye laser output (4%) is sent through a plane Fabry–Perot interferometer to provide precise frequency calibration lines. The interferometer with an invar spacer of 1.593 cm length is contained in a thermally insulated air filled housing. Corrected for the refractive index of air, the separation of adjacent marker lines is 9.414 GHz. In order to assure single line operation of the dye laser oscillator the spectral distribution of the laser output is continuously monitored by a solid quartz Fabry–Perot with a free spectral range of 17 GHz.

The marker signal and the detected benzene fluorescence are normalized to the intensity of the dye laser pulses by means of two laser spectroscopic detection systems (Molectron LSDS) and are recorded simulta-

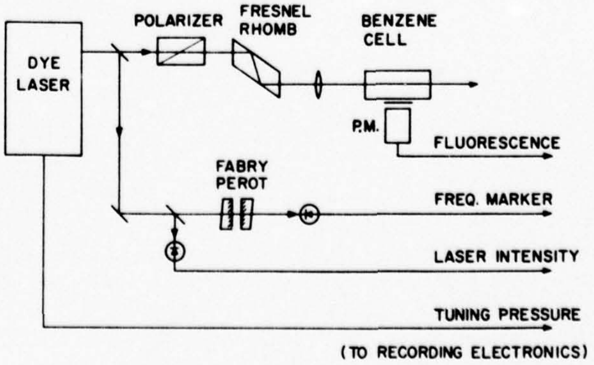

FIG. 1. Scheme of the experimental setup.

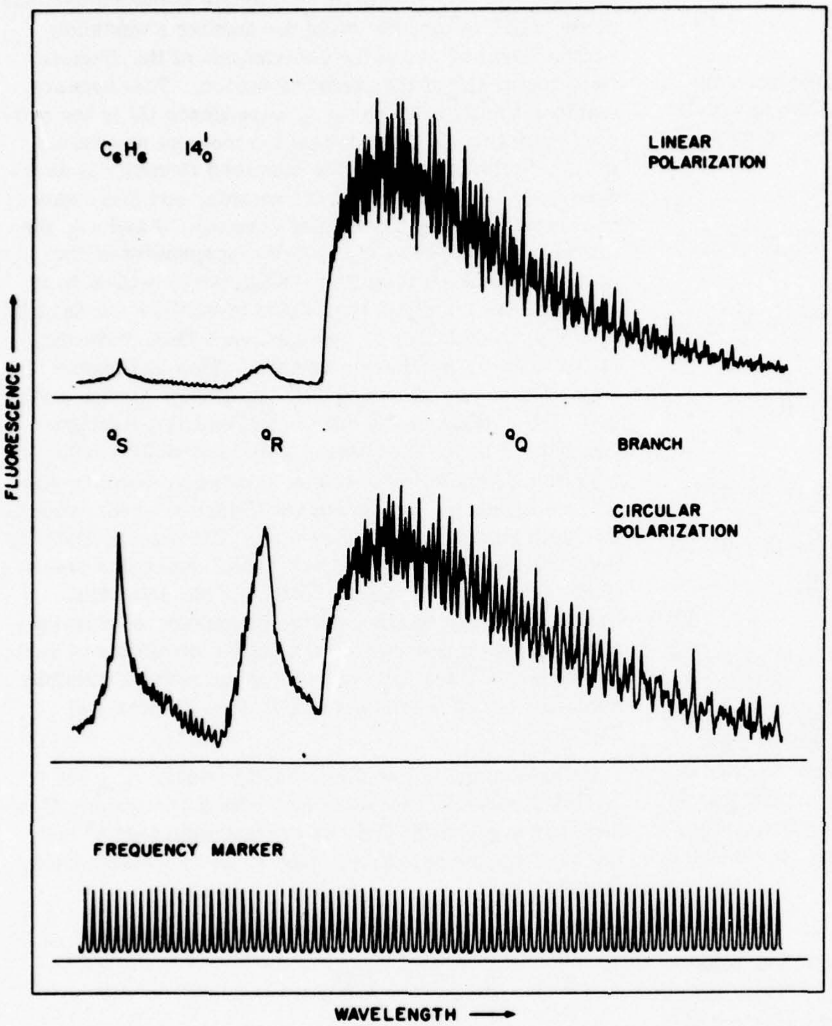

FIG. 2. Rotational structure of the ^QS, ^QR, and ^QQ branches of the b_{2u} 14_0^1 band of C_6H_6 excited with linear and circular polarized light. Simultaneously recorded frequency markers are provided by a Fabry–Perot with a finesse of about 10 (reflectivity–less than 90%) and 9.414 GHz free spectral range. The scan speed is 0.2 GHz/s and the time constant $\tau = 1$ s.

neously with two *xy* recorders. The *x* axis of both recorders are controlled and synchronized by the analog output of a Baratron pressure gauge (MKS-Instruments), which monitors the tuning pressure of the dye laser oscillator.

This pressure gauge has a resolution of 10^{-5} (at 1000 Torr). In the range of 10–760 Torr it is linear within one part in 10^3. Because the frequency tuning of the dye laser is proportional to the variation of the pressure of the tuning gas[10] this recording scheme provides a highly linear frequency scale which is unaffected by variations of the scan speed. With propane as scan gas a pressure change of 760 Torr tunes the laser frequency by about 575 GHz (4.8 Å) at 5000 Å.

As an example, Fig. 2 shows the spectrum of the two-photon excitation of the 14_0^1 band of C_6H_6 for linear and circular polarized light, together with simultaneously recorded frequency markers. The overall contours of both spectra as well as their rich rotational structure are discussed in detail in Sec. IV.

III. THEORY OF TWO-PHOTON SPECTRA OF SYMMETRIC ROTORS

Since the theory of two-photon spectra has been covered elsewhere, especially in the Raman literature,[11] we would like to review only a few aspects which are essential for two-photon excitation in the benzene molecule. In addition we will point out some implications which are not previously discussed but very useful in assigning two-photon spectra.

In two-photon excitation of benzene the rotational envelope may be altered drastically by changing the relative polarization of the two photons. This feature is absent in one-photon excitation. Because it is particularly easy to obtain strong laser beams which are linearly or circularly polarized, this polarization dependence of the band contours can be helpful in assigning and characterizing the observed spectra.

As is well known, the rotational selection rules for two-photon spectra are

$$\Delta J = 0, \pm 1, \pm 2 \ ,$$

$$\Delta K = 0, \pm 1, \pm 2 \ ,$$

where J is the total angular momentum quantum number, and $K \leq J$ is the projection of J along the molecular symmetry axis. With these selection rules we may write the rotational frequencies as

$$\nu = \nu_0 + \nu(n) + \nu(m) \qquad (1)$$

where ν_0 is the frequency of the vibronic origin of the band and $n = \Delta J$, $m = \Delta K$,

$$\nu(n) = (B' - B'')J^2 + [B'(2n+1) - B'']J + (n^2 + n)B' \ , \qquad (2)$$

and

$$\nu(m) = [(C' - B') - (C'' - B'')]K^2 + 2m(C' - B')K + m^2(C' - B'), \qquad (3)$$

where C and B are the rotational constants of the molecule (prime and double prime refer to excited and ground states, respectively). Since benzene is a planar oblate rotor $C = \frac{1}{2}B$; Eq. (3) is simplified to

$$\nu(m) = -\tfrac{1}{2}(B' - B'')K^2 - mB'K - \tfrac{1}{2}m^2B' \ . \qquad (4)$$

For transitions with $\Delta K = \pm 1$ or ± 2 we must also consider the possibility of a Coriolis effect due to the interaction of vibration and rotation. In benzene, this can only occur in the e_{1u} and e_{2g} vibrations since no other modes involve motion in the molecular plane capable of generating angular momentum about the symmetry axis. Two-photon transitions only occur to e_{1u} modes, so only for these transitions must we add a Coriolis term of the form

$$\pm 2C'K\zeta \ ,$$

where the upper sign refers to $\Delta K = +2$ or -1 and the lower sign to $\Delta K = -2$ or $+1$. ζ is the Coriolis parameter which measures the degree of coupling between vibration and rotation $(-1 \leq \zeta \leq +1)$.

The values of ΔK which appear in a particular band depend on the vibronic symmetry of the two states involved. The direct product of the irreducible representations to which the initial and final (vibronic) state belong must contain the irreducible representation of the tensor product of two dipole moment vectors. In benzene the ground electronic state is A_{1g} and the excited state is B_{2u}. Simple group theoretical considerations lead to the following table:

Electronic symmetry	Vibrational symmetry	Vibronic	ΔK
B_{2u}	b_{2u}	A_{1g}	0
B_{2u}	e_{2u}	E_{1g}	±1
B_{2u}	e_{1u}	E_{2g}	±2
B_{2u}	b_{1u}	A_{2g}	±2 (nonidentical photons only).

Thus assignment of ΔK immediately determines (or confirms) the vibronic symmetry of the observed band.

The values of ΔJ are determined mostly by the relative polarization of the two photons absorbed. This observation is perhaps the most important deviation from one photon spectroscopy. In one-photon spectroscopy the intensity of a transition in a single molecule depends on the relative orientation of the angular momentum vector with respect to the polarization of the electric field vector (**E**) of the absorbed photon. This appears mathematically through the M dependence (M is the projection of **J** on **E**) of the transition moment matrix elements.[12] However since the observed intensity is averaged over all molecules in the sample, and these have M values randomly distributed between $-J$ and $+J$, the intensity of each branch is totally independent of the polarization of exciting light. Observed spectral band contours are identical regardless of whether the light is linearly, circularly, or unpolarized. This, however, is not true for two-photon spectra. This is because both photons are absorbed simultaneously through a virtual state. Suppose one photon is linearly polarized along the Z space direction. This immediately selects a preferred direction in space, and the probability that the second photon is absorbed will depend on its orientation with respect to this direction. The total probability must still be averaged over all initial molecular orientations, however now the intensities of the individual branches depend on the relative orientation of polarization of the two photons. The relative intensities of various branches have been calculated for several possible combinations of photon polarization by Placzek and Teller.[13]

In these calculations the intensity factors $I_{M_1M_2}$ for $\Delta K = 0$ absorption of two photons with polarizations M_1 and M_2 are given in terms of the isotropic part G^0 and the quadrupolar anisotropic part G^2 of the polarizability tensor:

M_1	M_2	$I_{M_1M_2}$
0	0	$\frac{1}{3}G^0 + \frac{2}{15}G^2$
1	-1	$\frac{1}{3}G^0 + \frac{1}{30}G^2$
0	1	$\frac{1}{10}G^2$
1	1	$\frac{1}{5}G^2$.

G^0 and G^2 depend on J', K', J'', K''. G^0 is zero unless $J' = J''$ and consequently is important only in Q branches, while G^2 is nonzero for O, P, Q, R, S branches.

In our experiment both photons are either linearly polarized ($M_1 = M_2 = 0$) or circularly polarized ($M_1 = M_2 = 1$). And the ratio

$$I_{00}/I_{11} = \tfrac{5}{3}(G^0/G^2) + \tfrac{2}{3}$$

predicts that the Q branch ($G^0 \neq 0$) should be relatively more dominant in linearly than in circularly polarized excitation. This is exactly what is observed experimentally (Fig. 2) in all transitions to vibrations of symmetry b_{2u} ($\Delta K = 0$). For other values of ΔK, the ratios of the intensities do not vary from branch to branch for the two different polarizations of the exciting photons.

IV. ANALYSIS OF THE SPECTRA

In order to aid in the assignment of observed spectral features a computer program was written to calculate two-photon frequencies and intensities, and to plot the

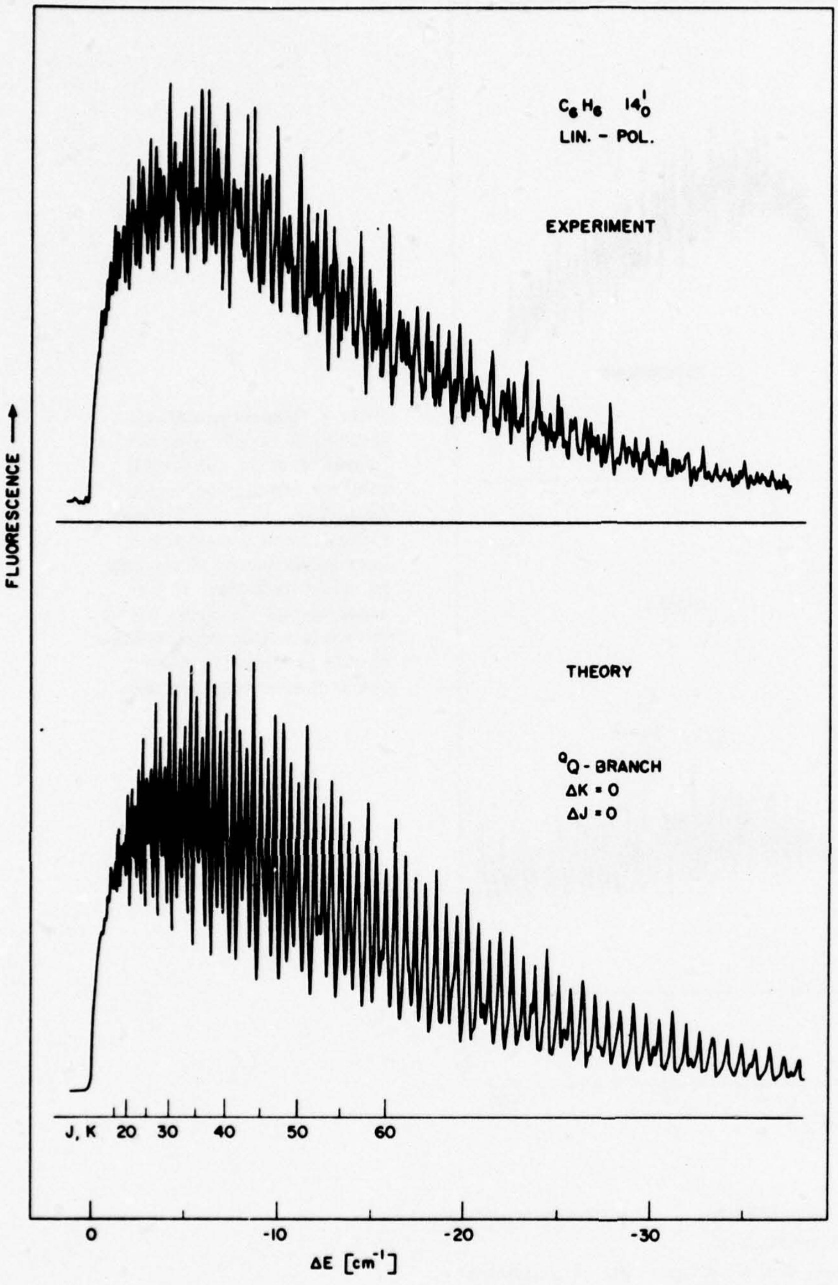

FIG. 3. Experimental and theoretical spectrum of the ^QQ branch of the b_{2u} 14_0^1 transition excited with linear polarized light. Some of the identified rotational transitions are labeled by their quantum number. For further details see text.

output on the same scale as the observed spectra. The program used Eqs. (1), (2), and (4) for frequencies, and the two-photon transition moment matrix elements from Condon and Shortley[12] multiplied by a Boltzmann factor to determine line intensities. Each line was given a Gaussian shape to approximate a Doppler profile with a half-width determined by estimation from observed spectra. ΔK selection rules were determined from the vibronic symmetry obtained from vibrational analyses.[3,4] As will be seen these selection rules give highly characteristic spectral profiles and thus may be viewed as confirmation of previous low resolution two-photon work. ΔJ selection rules, as noted above, depend partly on the type of polarization used, and where large differences were observed (mainly for $\Delta K = 0$, when both photons are linearly polarized as compared to both photons circularly polarized) separate fits were made.

Calculations were made on a PDP-10 and plotted with an on-line Calcomp XY10A plotter. The procedure was to assume a set of ground and excited state rotational constants (and Coriolis constant where appropriate) and perform a calculation of the spectrum. The calculated spectrum was compared with the observed spectrum, new values for the parameters were selected, and further calculations performed, until an optimum fit was obtained. During this procedure the line widths and

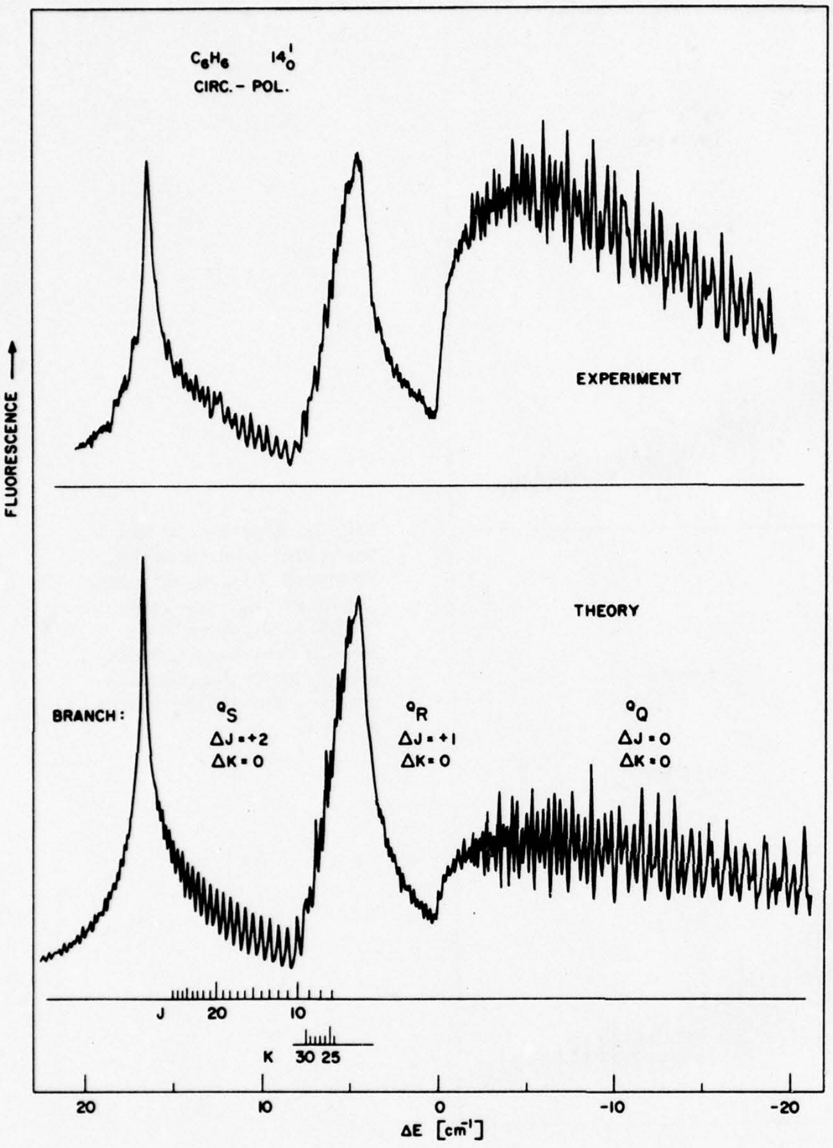

FIG. 4. Experimental and theoretical spectrum of the ^QS and ^QR branch of the 14_0^1 band for circular polarized excitation. Because the exciting light still contains a very small amount of linearly polarized radiation, in the experimental spectrum the ^QQ branch is a little more intense, as it is predicted by theory. For further details see text.

number of rotational levels included were adjusted for optimum visual fits. It was found that a linewidth of 0.04 cm^{-1} looked best, and that calculations including up to $J = 100$, $K = 100$ were sufficient. Inclusion of higher levels did not significantly alter the calculated contours, but did increase calculation times considerably.

Ground state rotational constants were taken from the Raman spectra of Stoicheff[11] and are listed in Table I. Initial guesses for the excited state rotational constants were taken from the one-photon ultraviolet absorption spectra of Callomon, Dunn, and Mills.[9] It was found that only changes in rotational constant on excitation significantly effect the observed spectra. Hence the values obtained for changes in rotational constant are independent of the accuracy with which the ground state levels are known.

Since deuterium substitution does not drastically effect the overall shape of the observed spectra, we shall discuss both C_6H_6 and C_6D_6 spectra together for each vibronic transition.

A. A_{1g} spectra

The A_{1g} spectra arise from combination of a b_{2u} (14_0^1) vibration with B_{2u} electronic state. For this vibronic

TABLE I. Rotational constants, structural parameters, and Coriolis constants in the $^1A_{1g}$ and $^1B_{2u}$ states of benzene.

Method	Raman spectroscopy[a]	One-photon uv absorption[b]	Two-photon[c]
$B(C_6H_6)cm^{-1}$	0.18960(5)	0.1810(5)	0.18134(5)
$B(C_6D_6)cm^{-1}$	0.15681(8)	0.1504(5)	0.15041(5)
r_{CC} (Å)	1.3974(10)	1.435(4)	1.4319(9)
r_{CH} (Å)	1.084(5)	1.07(2)	1.084(1)
$\zeta(C_6H_6)$	$+0.62(5)(\nu_6)$	$+0.60(5)(\nu_6)$	$+0.78(2)(\nu_{18})$
$\zeta(C_6D_6)$	$+0.43(5)(\nu_6)$	$+0.43(5)(\nu_6)$	$+0.62(2)(\nu_{18})$

[a] Reference 11. [b] Reference 9. [c] This work.

symmetry, $\Delta K=0$. In linear polarization the only strong transitions are $\Delta J=0$, and the spectrum consists almost entirely of a Q branch starting at the origin and shaded to the red with a series of regularly spaced intense peaks (Fig. 2).

It is found that the frequency separation of these peaks may be fit by a least squares procedure to a quadratic of the form

$$\nu=\nu_0-0.0166\, j^2\,, \quad (C_6H_6)$$

$$\nu=\nu_0-0.0128\, j^2\,, \quad (C_6D_6)$$

where j is an integer. It may easily be shown that the most intense lines in the spectrum should be those with $K\simeq J$ and from Eqs. (1)–(4) we may see that lines with common values of $J=J_0-k$ and $K=K_0-2k$ ($k=0, 1, 2, \ldots$) will be nearly coincident. Substituting $J_0=K_0$ we obtain

$$\nu=\nu_0+(B'-B'')(\tfrac{1}{2}J_0^2+J_0-k-k^2);$$

for small k and $J_0\gg 1$

$$\nu\simeq\nu_0+\tfrac{1}{2}(B'-B'')J^2\,,$$

from which we may obtain a tentative line assignment and initial guess for $B'-B''$. This guess is refined by the exact calculation procedure described above. The assignments may easily be confirmed by exact calculations using the optimum rotational constants. We may label each line by the value of $J_0=K_0$ as shown in Fig. 3 (also see Table II).

For circularly polarized spectra in addition to the Q branch, the $R(\Delta J=+1)$ and $S(\Delta J=+2)$ branches have appreciable intensity (Figs. 2 and 4). The S branch appears as a series of regularly spaced peaks to the blue of the origin which are composed of lines of the same J and low values of K, usually 0, 1, 2... We label these peaks with their J values (Fig. 4 and Table III). The peaks are spaced closer together to higher frequencies until they form a sharp head (at $J=44$ for C_6H_6 and J

TABLE II. Observed frequencies (cm^{-1}) in the ^{Q}Q branch of the 14_0^1 band of C_6H_6 and C_6D_6.[a]

J	C_6H_6 ν	C_6D_6 ν
17	−1.34	...
18	−1.52	−1.12
19	−1.60	−1.30
20	−1.84	−1.42
21	−2.07	−1.57
22	−2.23	b
23	−2.39	−1.78
24	−2.65	−1.98
25	−2.86	−2.18
26	−3.04	−2.40
27	−3.33	b
28	−3.54	−2.63
29	−3.75	−2.91
30	−4.07	−3.16
31	−4.35	b
32	−4.62	−3.41
33	−4.88	−3.73
34	−5.19	−4.01
35	−5.48	b
36	−5.74	−4.39
37	−6.10	−4.66
38	...	−4.88
39	...	−5.07
40	...	−5.31

[a] b–blended.

TABLE III. Observed frequencies (cm^{-1}) in the ^{Q}S branch of the 14_0^1 band of C_6H_6 and C_6D_6.[a]

J	C_6H_6 ν	C_6D_6 ν
7	5.84	4.73
8	6.30	5.20
9	6.95	b
10	7.58	6.12
11	8.11	6.67
12	8.51	7.2(b)
13	9.11	7.58
14	9.67	8.00
15	10.07	8.37
16	10.57	8.76
17	11.04	9.20
18	11.36	9.52
19	11.78	9.86
20	12.18	10.20
21	12.60	10.56
22	12.92	b
23	13.21	11.14
24	13.58	11.50
25	13.90	b
26	14.16	11.98
27	14.45	...
28	14.72	...
29	15.06	...

[a] b–blended.

TABLE IV. Observed frequencies (cm^{-1}) in the ^{P}P branch of the 17_0^1 band of C_6H_6.

J	ν
21	−5.90
22	−6.30
23	−6.64
24	−7.04
25	−7.40
26	−7.88
27	−7.27
28	−8.70
29	−9.16
30	−9.61
31	−10.10
32	−10.60
33	−11.09
34	−11.48
35	−11.93
36	−12.37
37	−12.87
38	−13.41
39	−13.90
40	−14.45
41	−14.90
42	−15.49

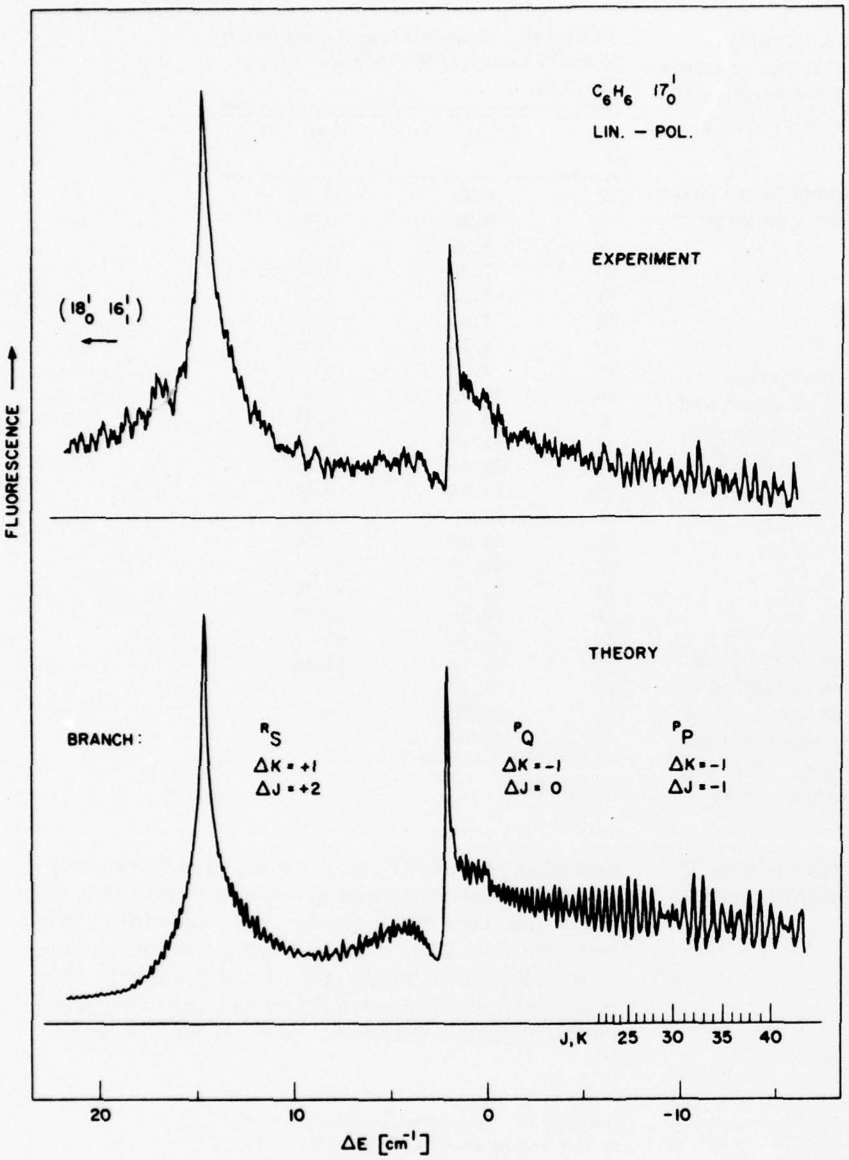

FIG. 5. Rotational structure of the e_{2u} 17_0^1 band in C_6H_6 excited with linear polarized light. The left part of the experimental spectrum is overlapped partly by a band identified as $18_0^1\,16_1^1$.[3]

$=46$ for C_6D_6). The R branch appears nearer the origin and is somewhat broader than the S branch. Several subband heads ($J=22$ for C_6H_6, $J=23$ for C_6D_6) can be identified on the blue edge of this peak and are labeled in Fig. 4 by their K value.

B. E_{1g} spectra

The E_{1g} spectra which have been observed arise from a combination of e_{2u} vibration (17_0^1) with the B_{2u} electronic state. The selection rules are $\Delta K=\pm 1$. The observed spectra (Fig. 5) consists of two sharp peaks to the blue of the origin and several regularly spaced less intense ^RS branch lines. The high frequency line is a sharply peaked but featureless pileup of a group of very intense R_S branch lines. Another intense line, nearer to the origin has a very sharp blue edge which is formed by a head of $J=K$ lines (head at $K=20$) of a ^PQ branch beginning at the origin. The onset of this branch appears as a shoulder on the red slope of the intense peak.

The regularly spaced peaks arise from a ^PP branch consisting of subbands with most intensity at $K=J$, and the lines are thus labeled with this value (Fig. 5 and Table IV).

C. E_{2g} spectra

The E_{2g} spectra comes from combinations of an e_{1u} (18_0^1) vibration with the B_{2u} electronic state. Selection rules are $\Delta K=\pm 2$, and we have the additional complication that the Coriolis effect must be considered. The observed spectra (Fig. 6) consists of a very intense peak to the blue which has a series of regularly spaced intense features running down its blue edge. Somewhat to the red of the origin are a series of regularly spaced but less intense features which resemble subband heads. Fortunately it was found that the latter are very sensi-

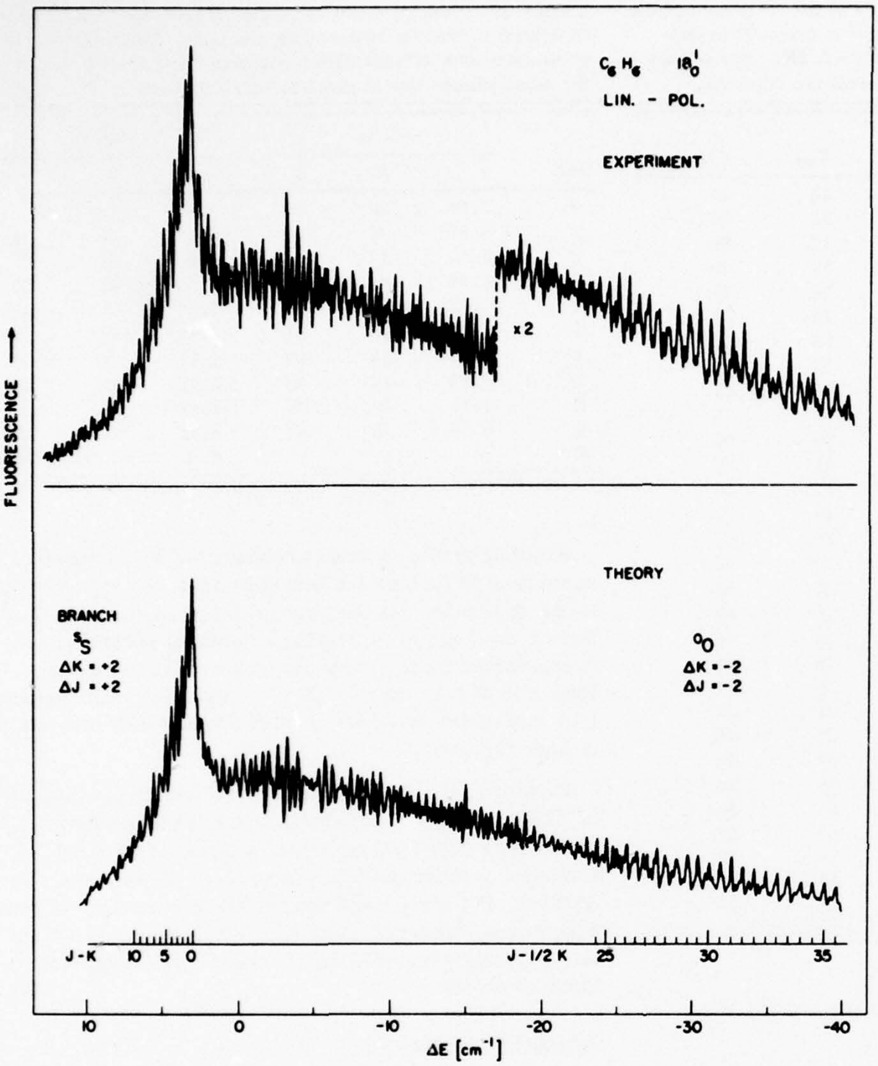

FIG. 6. Rotational structure of the e_{1u} 18^1_0 band excited with linear polarized light.

tive to ΔB and insensitive to the Coriolis constant while the former peaks are quite sensitive to the Coriolis constant. Hence, the fitting procedure was greatly simplified. The red peaks were readily fit using ΔB from other bands. They were found to arise from an $^O O$ branch ($\Delta K = -2$, $\Delta J = -2$). The heads were coincidences of lines with a common value of $J - 1/2K$ which tend to be closely spaced for planar molecules. For $B' \approx B''$ we find

$$\nu \approx \nu_0 - 4B'(J - 1/2K) .$$

The peaks are labeled by the pseudoquantum number $J - 1/2K$ (Fig. 6 and Table V).

The peak to the blue is composed of $^S S$ branch lines ($\Delta K = +2$, $\Delta J = +2$) formed from coincidences of lines for which $J-K$ is a constant. They are thus labeled by the pseudoquantum number $J-K$. The positions of these lines are very sensitive to the Coriolis constant and we are able to obtain very accurate values as a result. ($\zeta = 0.78 \pm 0.02$ for C_6H_6 and $\zeta = 0.62 \pm 0.02$ for C_6D_6) (Fig. 6 and Table VI).

V. STRUCTURE OF BENZENE IN THE $^1B_{2u}$ ELECTRONIC STATE

As can be seen from Figs. 2–6 the fits between profile and frequency of all major peaks is matched as is virtually every regularly spaced less intense peak. In all, several thousand features are matched with only two adjustable parameters (for each isotope), the rotational constant and the Coriolis parameter. Error limits for these parameters have been determined by varying them slightly until the observed fit is noticeably worse. Within experimental error all vibronic bands were fit by the same rotational constant. The results are listed in Table I, along with the results on the $^1A_{1g}$ ground state from Raman spectroscopy by Stoicheff[11] and previous results on the $^1B_{2u}$ state from one-photon ultraviolet absorption spectroscopy by Callomon, Dunn, and Mills.[9]

Owing to its high symmetry, the structure of the benzene molecule may be described by two parameters: the C–C distance and the C–H distance. These are re-

TABLE V. Observed frequencies (cm^{-1}) in the ^OO branch of the 18_0^1 band of C_6H_6 and C_6D_6. Each subband consists of coincidences of lines with a common value of $J-1/2K$. These lines form subband heads as indicated in the last two columns.

$J-1/2K$	C_6H_6 ν	C_6D_6 ν	K_{BH}	J_{BH}
21	...	−15.77	10	26
21 1/2	...	−16.29	11	27
22	...	−16.72	12	28
22 1/2	...	−17.25	13	29
23	...	−17.74	14	30
23 1/2	...	−18.27	15	31
24	...	−18.80	16	32
24 1/2	−23.67	−19.31	17	33
25	−24.28	−19.77	18	34
25 1/2	−24.92	−20.41	19	35
26	−25.62	−20.90	20	36
26 1/2	−26.28	−21.39	21	37
27	−26.95	−22.01	22	38
27 1/2	−27.65	−22.52	23	39
28	−28.30	−23.01	24	40
28 1/2	−28.95	−23.69	25	41
29	−29.72	−24.22	26	42
29 1/2	−30.42	−24.80	27	43
30	−31.16	−25.31	28	44
30 1/2	−31.88	...	29	45
31	−32.63	...	30	46
31 1/2	−33.42	...	31	47
32	−34.16	...	32	48
32 1/2	−34.94	...	33	49
33	−35.70	...	34	50
33 1/2	−36.47	...	35	51
34	−37.19	...	36	52
34 1/2	−38.03	...	37	53
35	−38.8	...	38	54
35 1/2	−39.62	...	39	55

lated to the moment of inertia about the sixfold symmetry axis I_B by

$$I_B = 3[m_c r_{cc}^2 + m_{\mathrm{H,D}}(r_{\mathrm{CC}} + r_{\mathrm{CH}})^2] ,$$

where $B = \hbar^2/2I_B$ is the experimentally determined rotational constant. We thus need only the rotational constants for two isotopes to completely determine the structure for a particular state. These results are also included in Table I. The results of this work are

$$r_{\mathrm{CC}} = 1.4319 \pm 0.0009 \text{ Å} ,$$

$$r_{\mathrm{CH}} = 1.084 \pm 0.001 \text{ Å} .$$

The value for the CH distance is identical to that of the electronic ground state, while the CC distance is larger by ~ 40 mÅ. While the values reported here are considerably more accurate, they fall within the error limits of the values of Callomon, Dunn, and Mills, and may thus said to be in agreement.

VI. CONCLUSIONS

The theoretical analysis of the rotational spectra of the b_{2u} (14_0^1), e_{2u} (17_0^1) and e_{1u} (18_0^1) vibrational levels in the $^1B_{2u}$ electronic state of C_6H_6 and C_6D_6 provide, for the first time, accurate rotational molecular parameters evaluated from highly resolved two-photon excited molecular spectra.

TABLE VI. Observed and calculated frequencies (cm^{-1}) in the ^SS branch of the 18_0^1 band of C_6H_6 and C_6D_6. Subbands consist of coincidences of lines with a common value of $J-K$. J, K of the most intense line is given for each subband.

	C_6H_6			C_6D_6		
$J-K$	ν	K	J	ν	K	J
0	3.24	26	26	...	...	...
1	3.57	24	25	3.72	30	31
2	3.89	22	24	3.95	28	30
3	4.24	20	23	4.19	26	29
4	4.62	18	22	4.52	24	28
5	4.97	16	21	4.82	22	27
6	5.35	14	20	5.07	20	26
7	5.73	12	19	5.35	18	25
8	6.18	10	18	5.58	16	24
9	6.55	8	17	5.83	14	23
10	...	...	...	6.18	12	22

Even higher accuracies are expected if the spectral resolution is further increased by reducing the linewidth of the dye laser. In the present laser system this can be achieved easily by placing a confocal resonator between oscillator and first amplifier.[7] The resulting linewidth of less than 0.003 cm^{-1} should permit Doppler-free molecular two-photon spectroscopy with exceedingly high resolution.

Furthermore, other bands, in particular b_{2u} (15_0^1) and e_{1u} (19_0^1), which are presently under investigation, should give more valuable information on coupling schemes, assignments and molecular parameters. In addition, the analysis of the rotational structure of some C_6D_6 bands, labeled Y_0^1 and W_0^1,[2] which so far could not be positively assigned, might confirm the suggested isotopic origin.[4]

ACKNOWLEDGMENTS

We wish to thank Professor A. L. Schawlow for his continuous stimulating interest in this research. And we are grateful to Professor W. M. McClain for several helpful discussions during the course of this work.

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†NATO Research Fellow.

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APPENDIX D.

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APPLICATIONS OF HIGH RESOLUTION LASER SPECTROSCOPY*

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Introduction

The advent of high monochromatic tunable laser sources has stimulated important advances in optical spectroscopy, as documented by several recent good reviews (1-3).

The highest resolution in optical spectroscopy is achieved by eliminating the Doppler broadening of atomic or molecular spectral lines. The classic approach is the transverse observation of a well collimated molecular beam, and quite spectacular results have been obtained by this method with the help of tunable lasers (4). But the high intensity of laser light has also led to the development of a variety of new nonlinear spectroscopic techniques, which permit Doppler-free observations of a simple gas sample. Saturated absorption spectroscopy (1-3,5-9) or Lamb Dip spectroscopy is the oldest and perhaps the most widely used of these methods. Here the spread of atomic velocities along the direction of observation is effectively reduced by velocity-selective bleaching and probing with two counterpropagating monochromatic laser beams. Saturated fluorescence spectroscopy (10) and in particular the sensitive technique of intermodulated fluorescence (11) extend the potential of this method to optically very thin fluorescent samples. The nonlinear interaction of two counterpropagating laser beams in a gas can also be detected via changes in the refractive index rather than in absorption, as demonstrated by saturated dispersion spectroscopy (12). Very recently we have developed a new technique, laser polarization spectroscopy (13), which achieves very high sensitivity by monitoring small changes in light polarization.

Other, different approaches to high resolution laser spectroscopy have been suggested, though not yet demonstrated. In particular it has been pointed out (14) that it should be possible to cool a gas sample very rapidly to a fraction of one Kelvin by resonant radiation pressure and hence to reduce the Doppler-width of its spectral lines. According to another suggestion (15) the random thermal motion

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of gas atoms could be eliminated by trapping of slow atoms in the nodes of a three-dimensional standing wave field. The possibility of combining radiation cooling and radiation trapping has also been discussed (16).

The need for cooling or velocity selection is circumvented in the perhaps simplest and most elegant approach to high resolution laser spectroscopy, the recently demonstrated and already widely used method of Doppler-free two-photon spectroscopy (17-20, 1-3). It complements the other techniques because of its different selection rules. The technique can in principle be generalized to multi-photon transitions (18), and Doppler-free three-photon spectroscopy has recently been demonstrated (20).

It is impossible within our limited space to discuss all the interesting applications of high resolution laser spectroscopy which have already been reported or suggested. This holds true even if we ignore such applications as chemical or isotope analysis, trace detection or pollution monitoring, where the high sensitivity of laser methods is often more important than the potential high resolution. The new techniques of Doppler-free spectroscopy are naturally of particular interest for detailed investigations of atomic and molecular energy levels, including their isotope shifts, fine and hyperfine splittings, Zeeman and Stark effect, light shifts or collision and pressure effects (1,2). Another very important application is the locking and stabilization of a laser wavelength to some atomic or molecular resonance line. Such lasers have already proven valuable tools for precision metrology and promise future new standards of length and time. High resolution laser spectroscopy has opened interesting new possibilities for basic physics research. The values of two fundamental constants, the speed of light (2) and the Rydberg constant (22), have already been dramatically improved using the new methods. Interesting test of special relativity are presently underway, in particular a precise study of the second order Doppler-effect due to the relativistic time dilation (23) and a new search for "ether drifts," i.e. for possible anisotropies in the vacuum velocity of light (24). Other experiments can be interpreted as tests of quantum electrodynamic calculations. They include the measurement of Lamb shifts in hydrogen (22, 25) and detailed studies of spontaneous emission under monochromatic excitation (26). A particularly ambitious future project is the proposed search for a possible very small (10^{-15} eV) energy difference between the excited levels of two isomeric molecules of left handed and right handed configuration which may originate from parity-violating neutral currents (27).

The subsequent chapters will review some recent applications of high resolution laser spectroscopy to the study of atomic hydrogen in our laboratory at Stanford University. During the past few years we have become increasingly interested in precision spectroscopy of hydrogen, because this simple atom permits fascinating detailed comparisons between experiment and theory. Three different nonlinear spectroscopic methods have so far been successfully used: Doppler-free two-photon spectroscopy, saturated absorption spectroscopy and polarization spectroscopy. A review of our most recent experiments will not only serve to illustrate these techniques and to discuss some of their characteristics, advantages and limitations, but also to point out some possible future improvements and extensions.

Doppler-Free Two-Photon Spectroscopy of Hydrogen 1S-2S

Doppler-free two-photon spectroscopy requires in principle only a very simple experimental setup: a gas cell is placed in a standing wave field which is generated by reflecting the output of a tunable laser back into itself. Atoms are excited from the ground state to some excited state of the same parity by absorption of two counterpropagating laser photons, whose combined energies provide the required excitation energy and whose first order Doppler shifts cancel [1-3,17-20].

The line width of the resulting narrow two-photon resonance is ultimately only limited by the nautral line width, although the second order Doppler-effect, collision effects, light shifts, the finite interaction time with the laser beams or the laser band width may impose larger practical limits. A possible drawback is the requirement of a rather intense, highly monochromatic laser, since the transition probability is proportional to the square of the light intensity and can be rather small in the absence of any near-resonant intermediate state. On the other hand, all atoms contribute to the resonant signal, not just a few with a selected velocity, as in almost all other methods of Doppler-free spectroscopy, and the two-photon excitation can often be monitored with very high sensitivity via the subsequently emitted fluorescent light. A dramatic increase in signal, although at the expense of resolution, can in some cases be achieved by near-stepwise excitation through some intermediate level with two lasers of different wavelength [28].

Ever since the new technique was first suggested, numerous authors have pointed out that a particularly interesting subject would be the transition from the 1S ground state of atomic hydrogen to the metastable 2S state (Fig.1).

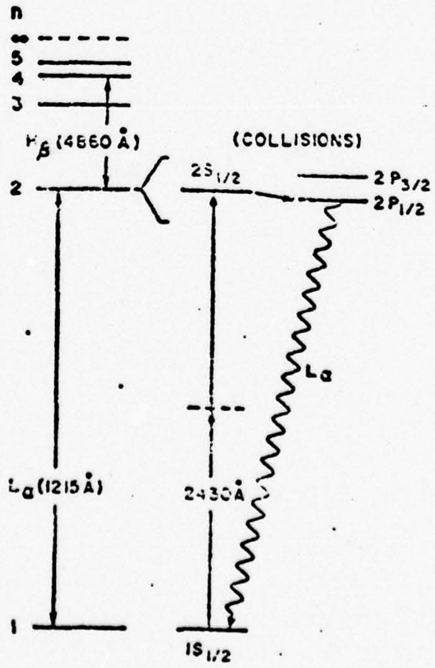


Fig. 1. Simplified term diagram of atomic hydrogen, illustrating Doppler-free two-photon spectroscopy of the 1S-2S transition. The Lyman-α and Balmer-β transitions are also indicated

In the absence of external perturbations, the upper 2S state decays via two-photon emission with a lifetime of about 1/7 sec, implying a natural line width of only about 1 Hz or an ultimate resolution limit of less than 1 part in 10^{15}. Even as long as the practical resolution remains far from this limit, spectroscopic studies of this transition open interesting new possibilities for precision measurements of fundamental constants and for tests of quantum electrodynamic calculations.

Unfortunately, such experiments require ultraviolet laser light at 2430Å, i.e. at twice the Lyman-α wavelength, which is somewhat difficult to generate with present tunable laser technology. For our experiments [28,25] we have employed a powerful pulsed dye laser oscillator-amplifier system, pumped by a 1 MW nitrogen laser, which provides peak powers on the order of 50 kW at the visible wavelength of 4860Å, with a line width of about 100 MHz, close to the Fourier-transform limit of its 10 nsec long pulses. Gas pressure tuning provides a continuous wavelength scan range up to several Å. The desired ultraviolet wavelength is generated by frequency doubling the visible laser output in a nonlinear crystal of lithium formate with an efficiency of 1-2%.

The scheme of our two photon spectrometer is shown in Fig. 2. The ultraviolet coherent radiation is focused into the observation chamber and a spherical mirror reflects the beam to provide the standing wave field. The hydrogen atoms are generated by dissociation of molecular hydrogen in a low pressure gas discharge. The two-photon excitation is observed by monitoring the subsequent emission of vacuum ultraviolet Lyman-α photons from the 2P state through a LiF window and interference filter with a solar blind photomultiplier. At the operating pressure of about 0.2 torr, collisions provide sufficient mixing between the 2S and 2P states for this observation scheme. At lower pressuresit would be necessary to apply a mixing static or radiofrequency field. An alternative would be the detection of charged particles which are produced by photoionization of the excited hydrogen.

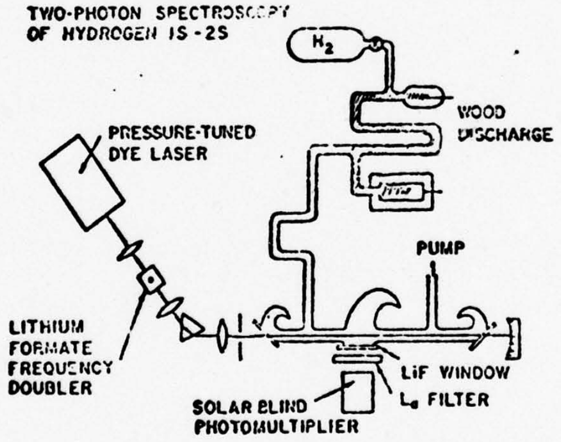


Fig. 2. Two-photon spectrometer for observation of hydrogen 1S-2S

Figure 3 shows some 1S-2S two-photon spectra obtained in this way.

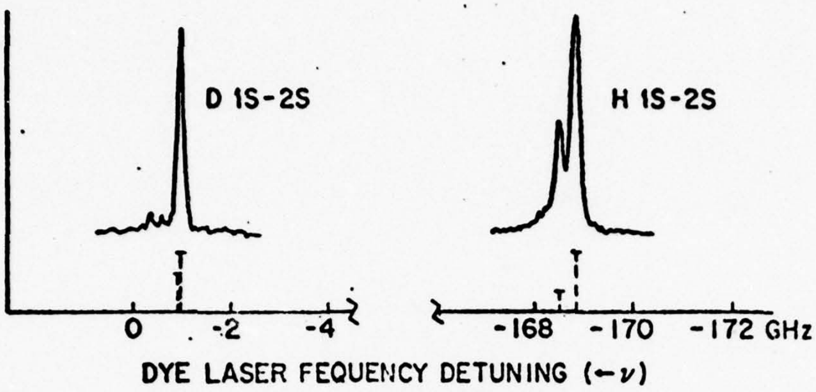


Fig. 3. Doppler-free two-photon spectra of the 1S-2S transition in atomic deuterium and hydrogen

The spectra were recorded in a mixture of deuterium and hydrogen, and the wide laser tuning range permitted a continuous scan over the large isotope shift. The line width is less than 2% of the Doppler width and is limited only by the exciting laser. Light shifts and transit time broadening are expected to be less than 1 MHz, and the second order Doppler effect contributes a line broadening of only about 50 kHz at room temperature. The spectrum of light hydrogen reveals the expected hyperfine doublet, the corresponding structure in deuterium is unresolved.

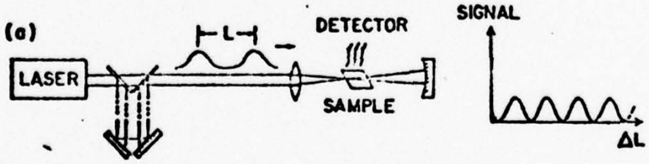
Depite the relatively large laser band width, these spectra provided a new value of the Lyman-α isotope shift which exceeds the accuracy of earlier measurements in the vacuum ultraviolet by several orders of magnitude. This improvement is not only due to the superior resolution, but also due to the fact that all wavelengths can now be measured conveniently in the visible. The measured 1S-2S isotope shift, 670.933±0.056 GHz agrees within its error limits with the theoretical prediction, 670.9949±0.008 GHz. If the experimental precision could be improved by a factor of 100, it would exceed the theoretical accuracy. The latter is limited by our knowledge of the ratio of electron mass to proton mass, and the envisioned more precise isotope shift measurement would in fact confirm or improve the value of this important mass ratio. It would also be interesting to precisely measure the absolute wavelength of the 1S-2S two-photon resonance. Even the present limited resolution should be sufficient to determine a new, more accurate value of the Rydberg constant.

There are several possible approaches to markedly improve the resolution of the 1S-2S two-photon spectrum. The most straightforward one would be the replacement of the transform-limited pulsed laser by a cw source of tunable radiation. Although cw dye lasers can operate at 4860Å, there is unfortunately at present no known nonlinear optical material which would permit the efficient 90°-phase-matched second harmonic generation at this short wavelength. But it is possible to generate 2430A radiation as the sum frequency of two different laser wavelengths in a crystal of ADP, cooled to near its Curie temperature [29]. CARL WIEMAN and JIM ECKSTEIN, two graduate students in our laboratory, have already succeeded in generating about .1 mW at 2430A in a single frequency in this way, by summing the output of a 500 mW Kr^+

laser at 4131Å and a 200 mW rhodamine 6G dye laser in a 5 cm long ADP crystal at 160 K. This power may be sufficient for a detectable two-photon excitation, if the gas sample is placed inside an intensity-enhancing confocal resonator. A remaining problem would be the line broadening due to the short transit time of the moving atoms through the required narrow beam waist.

A rather ingenious solution to the transit time problem has recently been suggested by CHEBOTAEV [30]. In the proposed scheme an atomic beam would be sent through two consecutive transverse standing wave fields. After interacting with the first field, the atoms will be found in a coherent superposition of states, i.e. they will oscillate at the two-photon resonance frequency, even though there is no observable dipole moment at this frequency. Depending on the phase of this oscillation relative to the second light field, the atoms entering the second field will be either further excited or they will return to the ground state by stimulated two-photon emission. It should thus be possible to observe the optical analog of the well-known Ramsey fringes which are routinely utilized in radiofrequency spectroscopy of molecular beams. The resolution would then be limited by the travel time between the two fields rather than by the transit time through each waist. The Doppler-free two-photon excitation ensures that the unavoidable spread of transverse atomic velocities together with the short light wavelength do not lead to random relative phases which would smear out any fringe structure, if single-photon excitation was attempted.

Similar "Ramsey fringes" should also be observable with a pulsed laser source, and without need for an atomic beam, if a gas cell is irradiated by two sequential phase-coherent standing wave light pulses. The spectral resolution would then be limited by the separation between the two pulses rather than by the pulse width. Experimentally this would require only a minor modification of the previously described, two-photon spectrometer. As shown in Fig. 4a, a second, delayed laser pulse could be provided by the same



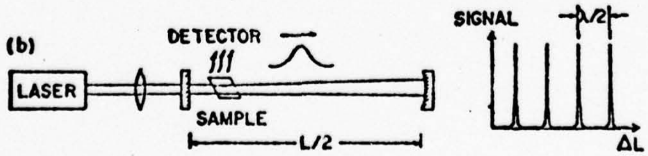


Fig. 4a. Doppler-free two-photon excitation with two phase-coherent light pulses. The excitation probability depends on the delay L between the two pulses. The pulse light is not drawn to scale. Each pulse has to be long enough to provide a standing wave field at the sample

Fig. 4b. Doppler-free two-photon excitation with a train of phase-coherent pulses. The sample is placed inside an optical resonator and a single light pulse is bouncing back and forth between the mirror. Sharp signal peaks rather than sinusoidal Ramsey fringes are expected pulsed laser with the addition of some beamsplitters and mirrors. The phases of the observed fringes will then be determined by the exact length of the optical delay line. But the expected sinusoidal Ramsey fringes would make the observation of any more complicated spectral structure rather difficult. In a way such an experiment can be considered as the analog of the diffraction of light at a double slit.

At Stanford we are presently working at another approach which corresponds to the optical diffraction at a multiple slit or diffraction grating. We are attempting to observe Doppler-free two-photon excitation by a whole train of phase coherent pulses. Multiple interference should then lead to sharp resonant peaks, if the excitation signal is recorded versus the pulse separation. A very simple way of generating such a pulse train is illustrated in Feg 4b. The sample is placed inside an optical resonator near one mirror, and a laser pulse is injected into this cavity, either through a partially transmitting end-mirror or better with the help of some active "inverse cavity dumper" to avoid high losses. The expected sharp "multiple-pulse Ramsey fringes" can be interpreted as originating from the modes of the optical resonator. The interpretation of the spectrum with its multiple orders can then proceed along the lines of conventional high resolution Febry-Perot interferometry. But unlike a passive filter interferometer, our resonator with actively injected pulse does not throw away any light. On the contrary it makes much more efficient use of the light than would be possible in a single-pulse experiment. As long as relaxation can be neglected, the probability of two-photon excitation for small intensities is proportional to the square of the number of pulse roundtrips, i.e. if the pulse recurs a hundred times, the two-photon signal at resonance should increase ten thousandfold. This enhancement should permit it to operate with large beam diameters to alleviate the problem of transit time broadening. As an additional benefit, such a scheme would reduce any light shifts, in particular if the pulse is short compared to the cavity length so that the atoms oscillate during much of the time in the dark at their undisturbed eigenfrequency. We expect that a resonator length of 2m will be sufficient to approach the resolution limit of 50 kHz which is set in hydrogen by the relativistic Doppler effect.

Saturated Absorption Spectroscopy of the Balmer-β Line

The successful observation of the hydrogen 1S-2S two-photon resonance with a frequency-doubled dye laser has opened the possibility for another very interesting experiment: the simultaneous observation of the Balmer-β line, i.e., the n=2 to n=4 transition (see Fig 1), with the fundamental dye laser output. If Bohr's formula were correct this latter interval would be exactly equal to 1/4 the Lyman-α interval, and we would find the two resonances at exactly the same dye laser frequency. The actual displacement is due to relativistic and quantum electrodynamic corrections plus some small nuclear structure effects. And the accurate comparison of the two optical energy intervals is providing for the first time an opportunity to precisely measure these level corrections. Such a measurement is in particular a sensitive test of the Lamb shift of the hydrogen ground state, which cannot be observed by radiofrequency spectroscopy, because there is no nearby P reference level. By recording a simple Doppler-broadened absorption spectrum of the Balmer-β line in a Wood-type gas discharge we were able to obtain first preliminary values of the 1S Lamb shift for hydrogen and deuterium (28). An improvement in the resolution by some method of Doppler-free nonlinear spectroscopy was then a very desirable next step.

To obtain a high resolution spectrum of the Balmer-β line, we decided to use the same method of saturated absorption spectroscopy which we had used earlier to resolve the fine structure of the red Balmer-α line and to determine a new value of the Rydberg constant from its absolute wavelength [22]. The scheme of this method is meanwhile well known: part of the visible dye laser output is split into a weak probe beam and a stronger saturating beam which are sent in opposite directions through the absorbing gas. Each monochromatic beam is generally absorbed by a different group of atoms, those with the right axial velocity to be Doppler-shifted into resonance. At the center of a Doppler-broadened absorption line, however, the two counterpropagating beams are resonantly interacting with the same atoms, those with zero axial velocity, and the saturating beam can bleach a path for the probe. To detect small bleaching, the saturating beam is chopped, and the synchronous modulation of the probe is recorded with a phase-sensitive detector. To further reduce the noise due to laser intensity fluctuations it has proven useful to use a second "dummy" probe beam, which does not cross the bleached region, in a differential detection scheme.

Figure 5 shows a saturation spectrum of the Balmer-β line in hydrogen

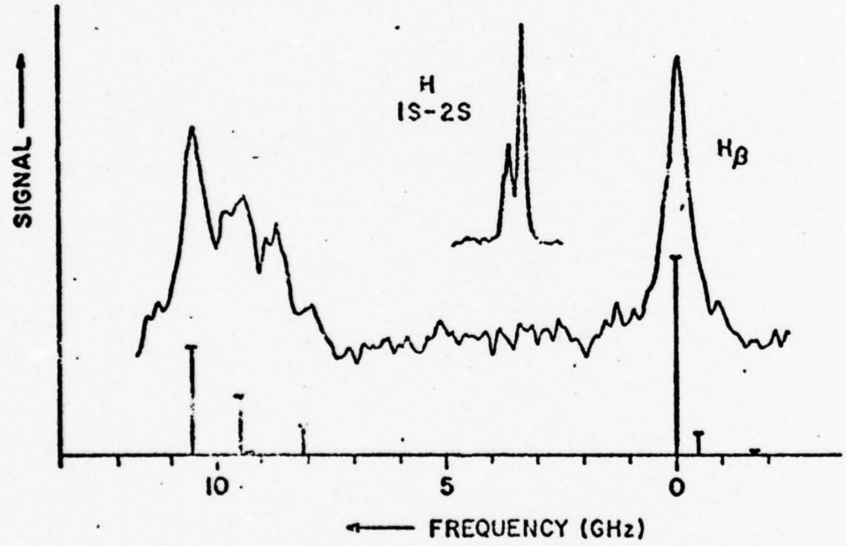


Fig. 5. Saturated absorption spectrum of the hydrogen Balmer-β line with theoretical fine structure spectrum, and simultaneously recorded 1S-2S two-photon spectrum

which was in this way recorded simultaneously with the 1S-2S two-photon spectrum (25). If the 1S state were not shifted above its Dirac-position by the Lamb shift, the two-photon spectrum would appear displaced to the left by about two scale divisions. By measureing the relative line positions and comparing them with their theoretical values, we were able to determine a 1S Lamb shift of 8.20±0.10 GHz for hydrogen and 8.25±0.11 GHz for deuterium. Both shifts agree within their error limits with the respective theoretical values of 8.14943(8) GHz and 8.17223(12) GHz. For hydrogen our result represents the first measurement of the ground state Lamb shift; for deuterium it offers a tenfold improvement over a determination by HERZBERG (31), which was based on a difficult absolute measurement of the vacuum ultraviolet Lymann-α wavelength.

The main limitation of the quoted accuracy is the obviously poor resolution of the Balmer-β saturation spectrum. A number of causes contribute to the large observed line widths which substantially exceed the 100 MHz laser bandwidth. A residual Doppler-broadening of about 50 MHz originates from a small finite crossing angle between the probe beam and the saturating beam. In order to obtain an acceptable signal-to-noise ratio it was necessary to operate at relatively high optical densities i.e. at high discharge currents, implying excessive Stark broadening in the discharge plasma. It was also necessary to work with laser intensities near or above the saturation intensity so that substantial power broadening was unavoidable. Particularly troublesome uncertainties in the line positions result from unresolved "cross-over" resonances which are expected halfway in between any two line components which share a common upper or lower level.

All these difficulties made it desirable to find a different, more sensitive method of high resolution laser spectroscopy. Intermodulated fluorescence spectroscopy [11] unfortunately does not offer any sensitivity advantage for a study of the Balmer-β line because the weak fluorescence from the laser-excited n=4 atoms is almost completely obscured by a strong background of spontaneous emission from the gas discharge. Moreover this method requires both laser beams to be sufficiently strong to saturate and it would thus aggrevate the problem of power broadening.

Doppler-Free Laser Polarization Spectroscopy

The problems encountered in saturated absorption spectroscopy of the hydrogen Balmer-β line provided the motivation for the development of the new, sensitive technique of laser polarization spectroscopy [13] which will be discussed in this concluding chapter.

A laser polarization spectrometer, as shown in Fig. 6, requires only minor modifications of a conventional saturation spectrometer. Again the output

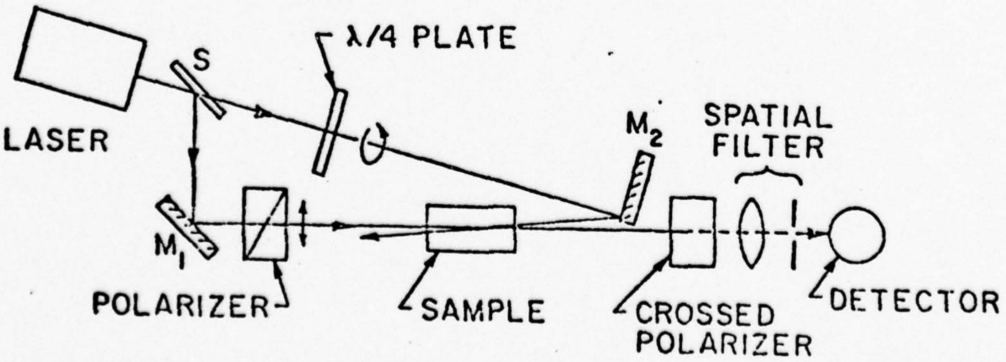


Fig. 6. Laser polarization spectrometer

of a tunable laser is split into a probe beam and a saturating beam. But this time, the probe is sent through a gas sample between crossed or nearly crossed linear polarizers so that only a small fraction of its light reaches a photodetector. The saturating beam is made circularly polarized by a quarter-wave plate and is sent in opposite direction through the sample. Since the absorption cross section for circularly polarized light depends generally on the orientation of the atomic angular momentum relative to the direction of light propagation, bleaching and optical pumping by the saturating beam will lead to a velocity-selective atomic orientation. The sample thus becomes optically anisotropic and is able to change the polarization of the probe light. Such a polarization change can be detected with high sensitivity via the change in light flux reaching the detector.

As in saturated absorption spectroscopy, a resonant signal is expected only near the center of a Doppler-broadened absorption line where the two counterpropagating beams are interacting with the same atoms. But in this older technique, the signal appears as a small intensity change on a much stronger background which carries obscuring noise and fluctuations. Polarization spectroscopy offers high sensitivity because it permits a very effective supression of this background. An improvement in signal-to-noise ratio of 100 - 1000 is quite readily achieved in practice under otherwise identical conditions. The new technique is thus of particular interest for studies of optically thin samples or weak lines or for measurements with weak or fluctuating laser sources.

For a more quantitative description, the probe beam can be decomposed into a right hand and a left hand circularly polarized component. At low intensities these components can be considered separately. Each experiences a light-induced change in absorption coefficient, $\Delta\alpha$, which, in the limit of a large Doppler width, is given by a Lorentzian function of the laser frequency with the natural line width. But the magnitude of this saturation effect is different for the two polarizations. The resulting dichroism will make the probe light elliptically polarized, as illustrated in Fig. 7. The Kramers Kronig relation requires corresponding different light-induced changes of the refractive index, Δn, for the two components. The resulting gyrotropic dichroism follows a dispersive function and will rotate the axis of the probe polarization as indicated at the bottom of Fig. 7 for some exaggerated anisotropy.

If the probe light is analyzed with a perfectly perpendicular polarizer, the transmitted light flux is given by the square of the horizontal projection of the probe field vector. It is a Lorentzian function of the laser frequency and corresponds to the natural absorption line, without Doppler broadening. An example of such a signal is shown in Fig. 8(a). If the analyzer is slightly rotated from its perpendicular position, the detector will register some finite background but the light flux is now sensitive to the sign of the polarization rotation and one obtains a dispersive resonance, as illustrated in Fig. 8(b). This latter signal is almost entirely due to the induced birefringence. It is proportional to the light-induced anisotropy, whereas the former is a quadratic function and becomes negligible for very small absorption depths or saturating intensities. It is obvious that such a dispersive signal is ideally studied for the locking of the laser frequency to some atomic or molecular resonance line. It is also possible to electronically record the first derivative of the dispersive signal by frequency modulating the laser and using a phase sensitive detector for the probe signal. The resulting resonance is non-Lorentzian, as shown in Fig. 8(c), but, quite remarkably . exhibits a line width less than half the natural

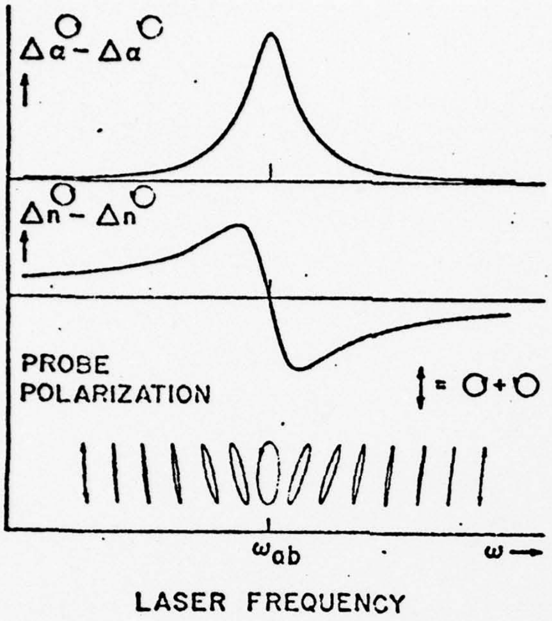


Fig. 7. Optical anisotropy in Doppler-free laser polarization spectroscopy versus laser frequency. The originally linearly polarized probe beam is decomposed into a right hand (↻) and a left hand (↺) circularly polarized component which experience different changes in absorption coefficient, Δα (top), and in refractive index, Δn (center). The polarization of the probe light after passing through the sample is shown at the bottom

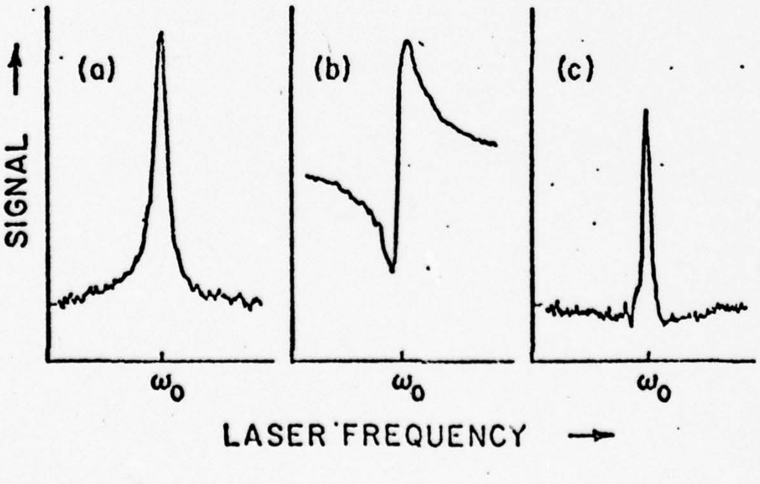


Fig. 8. Polarization spectra of the $2P_{3/2}$-$4D_{5/2}$ component of the hydrogen Balmer-β line, observed with a cw dye laser.
(a) Lorentzian signal, recorded with perfectly crossed analyzer
(b) Dispersive signal, observed with slightly rotated analyzer
(c) Derivative of dispersive signal (b)

width, i.e. it permits one to resolve line components which are separated by less than their natural width without the need for troublesome deconvolution.

To observe the hydrogen Balmer-β line in a Wood gas discharge by the method of polarization spectroscopy, we used a single-frequency cw Coumarin dye laser, pumped by a UV argon laser, with an (unstabilized)line width of about 10 MHz and a continuous scan range of 4 GHz (13). Standard Glan Thomson prism polarizers for the probe beam reach an extinction ratio of better than 10^{-7}, if residual stress birefringence in the quartz windows of the discharge tube is compensated by gentle squeezing with adjustable clamps. The resulting high sensitivity permitted us to operate at low laser power (less than 1 mW) as well as at low discharge current and gas pressure, thus eliminating many of the problems of the earlier saturated absorption experiment. It proved even feasible to make the two counterpropagating beams truly collinear and thus to avoid any residual Doppler-broadening, by replacing the mirror M_2 in Fig. 6 by a beam splitter, despite the relatively large laser intensity fluctuations resulting from feedback of light into the resonator.

The best spectra were obtained by recording the derivative of dispersive-resonances, as in Fig. 8 (c). A portion of the Balmer-β spectrum, recorded in this way, is shown in Fig. 9. The three strongest fine structure components are indicated in the level diagram on top, and the positions of the cross-over lines due to a common upper or lower level are indicated by arrows. The spectrum exhibits many more components which have to be ascribed

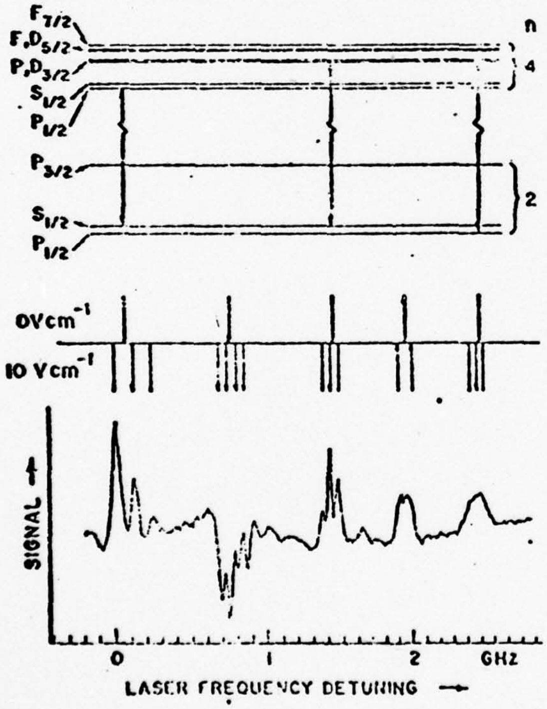


Fig. 9. Polarization spectrum of a portion of the deuterium Balmer-β line, corresponding to the line group at the right hand side of the saturation spectrum in Fig. 5. The three strongest fine structure comnents and the positions of the strongest Stark components for an axial electric field of 10 V/cm are shown on top for comparison. The positions of cross-over lines due to a common upper (↑) or lower (↓) level are indicated by arrows

to the Stark effect in the axial electric field of the positive discharge column. The splitting of the closely spaced fine structure levels in the n=4 state is essentially a linear function of the field and can be calculated exactly by diagonalizing the Hamiltonian. The calculated Stark pattern for a field of 10 V/cm agrees well with the observed spectrum. The inverted lines in Fig. 9 represent cross-over lines with inverted polarization rotation.

The observed Stark pattern changes quite drastically if the laser beams are laterally displaced from the tube axis, indicating the presence of radial electric fields due to volume and surface charges. Polarization spectroscopy is thus, for the first time, providing a way to accurately map the electric field distribution inside a low pressure gas discharge. This ability is of course extremely welcome for our intended precision spectroscopy because it permits us to make any necessary corrections for Stark shifts.

The spectrum clearly reveals the different line widths for components originating in the short living 2P state and in the metastable 2S state. The narrowest observed width is about 40 MHz and is limited by the finite laser band width and by factors like residual Stark broadening. The third component from the left corresponds to a transition from the 2S state to the long-living 4S state and would be forbidden in the absence of an external electric field. The natural line width of this component at low fields should be only about 1 MHz.

Polarization spectroscopy of the Balmer-β line is thus offering an interesting alternative to Doppler-free two-photon spectroscopy of the 1S-2S transition for the determination of the electron-proton mass ratio from the H-D isotope shift and for future precise measurements of the Rydberg constant. A combination of the two experiments promises a vastly improved value for the hydrogen ground state Lamb shift and should provide a very stringent test of quantum electrodynamics.

We have seen that the powerful new methods of nonlinear high resolution laser spectroscopy have opened numerous opportunities for interesting spectroscopic research, even if we restrict our attention to the simplest of all atoms. Naturally a much richer field lies ahead if we think more generally about atomic and molecular spectroscopy, although the wealth of potential information may then be much harder to digest. In this context we should note that the new techniques do not only provide "magnifying glasses" for the study of very fine spectral details but that they can also be immensely useful tools for more qualitative survey work. The techniques of saturated absorption spectroscopy and polarization spectroscopy can for instance be applied to unravel the complexities of molecular spectra by identifying lines which originate in a common level, as demonstrated in recent studies of Na_2 by lower level labeling [31] and by polarization labeling [32].

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APPENDIX E.

Frederic Ives Medal Address
October 1976
[Submitted to *Journal of the Optical Society of America*]

Lasers, Light and Matter[*]

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Stanford University

ABSTRACT

The nature of light can be known and understood only through its interactions with matter. A few of the new ways that lasers can extend our knowledge of these interactions are discussed. They include methods for eliminating Doppler broadening from thermal motions in gases, such as saturated absorption and polarization spectroscopy. A convenient digital wavemeter for measuring wavelengths of tunable lasers is described. Complicated absorption spectra can be simplified by using a laser to modify the population or polarization of the chosen lower level.

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An editorial in a recent issue of a leading optics journal[1] included the following remarkable statement: "The physics of light is by now pretty well understood and the real interest is in applying this knowledge for useful purposes, i.e., engineering." One might be tempted to dismiss this as harmless hyperbole from an editor who wishes to attract more eningeering papers to his journal. Yet it is uncomfortably close to what we are told by our colleagues in particle physics! So optical physicists need to ask themselves whether they believe that the physics of light really is well understood.

Certainly a great deal is understood. Maxwell's equations describe the wave properties of light very well. From them, using approximations like scalar waves or rays, the behavior of all optical instruments made of lenses, mirrors and apertures can be predicted. For such applications all we need to know about matter is that it refracts, reflects and absorbs light.

But everything we know about light comes from its interactions with matter. Thus these interactions really define what we mean by "light." They can be much more complex than just broadband refraction, reflection and absorption.

To be sure, we also have had since the 1920's the very good theory of quantum mechanics, extended in the 1940's to include quantum electrodynamics. These theories have been tested many times and in many ways and appear to describe atoms and their interactions with light very precisely. As far as we know, their laws also apply to molecules and larger aggregations of matter, but exact calculations are still not possible for anything beyond the simplest atoms and molecules. They cannot yet tell us exactly at what wavelength and how strongly a given substance absorbs or emits light. It should not be forgotten that the task of physics is to understand all matter and not just the hydrogen atoms. In the past we have found surprising phenomena in complicated atoms, molecules and condensed matter that were not at all evident from the basic laws. Moreover, we want to know what matter can be made to do as we arrange or excite it in new ways.

Fortunately, nature has provided us with the great analog computer, experiment. Technology has provided powerful tools. With lasers, we now are finding possibilities and many new ways to probe deeply the nature of matter and its interaction with light. These ways are far too numerous and varied to even list here, and many very clever researches are providing us with surprises. Instead, I should like to describe just a few of the things that we have been doing at Stanford lately, which may be in some measure representative of what can be done.

The light produced by lasers differs from that of other sources in that it is more, and sometimes enormously more powerful, directional, monochromatic and coherent. These properties determine the kinds of applications, scientific or technological, for which lasers can be used. Monochromaticity is the only one of these four basic properties needed to do absorption spectroscopy, if it is coupled with some tunability. Early lasers were hardly tunable, their wavelengths being determined by the emission lines of the particular substances used. As more tunability was achieved by various methods, that alone was sufficient to permit enormous advances in infrared spectroscopy. Previously there had been no way to get detectable amounts of highly monochromatic infrared light, since thermal radiators emit so weakly at those long wavelengths.

While monochromaticity is important for laser spectroscopy, the other properties of laser light can also be extremely useful. Coherence is used in important ways in stimulated Raman and Brillouin scattering, but is not essential in the methods that I am going to discuss.

The intensity of light in a laser beam can easily be high enough that it appreciably changes any matter that absorbs it. It can do this, even at relatively modest power levels, by partially saturating the absorption. That is, those atoms which have absorbed a light quantum are momentarily removed from their initial state. The absorption for that wavelength is reduced, at least until some relaxation process can replenish the supply of atoms in the particular absorbing state.

Saturation of absorption was familiar from radiofrequency and microwave work, but the ways it can be used in optical spectroscopy are many and wide-ranging. One important class of uses is in overcoming the Doppler broadening which so often obscures fine details of the spectra of free atoms and molecules. As is well known, atoms or molecules that are free and undisturbed are almost inevitably moving with high thermal velocities. Because of the Doppler effect, those atoms moving toward the observer appear to emit or absorb light of a higher frequency than those at rest. Receding atoms emit or absorb a lower frequency. Thus, in a gas with atoms moving in all directions, the spectral line is spread out over a range of wavelengths, typically about one part in 10^5. As tunable lasers can without great difficulty be monochromatic to one part in 10^8 or less, there is much information to be gained if Doppler broadening can be eliminated. The individual atom still retains its spectral fine or hyperfine structure, although it is nearly hidden by overlapping with spectra of other atoms moving in different directions. For forty years or so, atomic beams have been used to select just a group of atoms moving nearly perpendicular to the observer's line of sight, and they are still useful. Now, however, the intensity of lasers makes possible ways of eliminating Doppler broadening without using atomic beams.

The first step was the realization by Willis Lamb[2] that the two waves traveling in opposite directions inside a laser could work together to saturate the emission of those atoms which happened to have a zero component of velocity along the laser axis. Thus the power output would decrease when the laser length was adjusted to produce the light wavelength that would interact with those stationary atoms. This Lamb dip was soon observed by R. A. Macfarlane, W. R. Bennett, Jr., and Lamb.[3] It was used for high-resolution spectroscopy by A. Szöke and A. Javan,[4] but it was limited for some time to studying the laser transitions themselves or those few molecular lines which happened to coincide with gas laser wavelengths.

In 1970, T. W. Hansch[5] at Stanford and C. Bordé[6] in Paris independently proposed a method of using saturation to eliminate Doppler broadening, that did not require the sample to be placed inside the laser resonator. In the Hänsch-Bordé method (Fig. 1), the light from a tunable laser is divided by a beam splitter into a strong saturating beam and a weaker probe beam that traverse the absorbing gas along the same line but in opposite directions. (The angle between the beams is greatly exaggerated in the figure to keep them distinct.) When the saturating beam is on, it bleaches a path through the cell, and a stronger probe signal is received at the detector. As the saturating beam is alternately stopped and transmitted by the chopper, the probe signal is modulated. But that happens only when both beams interact with the same atoms, and those can only be atoms which are standing still or at most moving transversely. Thus this method picks out those atoms which have zero component of velocity along the laser beam directions, and ignores others. It could be said that the saturating laser marks a particular group of atoms by reducing their number, so that they can be recognized by the probe laser.

About the same time, broadly tunable visible lasers began to become available, most especially dye lasers, but the simple tunable lasers did not give narrow enough spectral lines. Hänsch[7] introduced a telescope and an etalon into the resonator of a pulsed dye laser and obtained band widths as narrow as 300 Megahertz or one part in 2×10^6. Further narrowing was obtained as needed by a confocal interferometer used as a passive filter.

With this broadly tunable, narrow line laser and the external saturation method, Hänsch and Shahin were able to apply Doppler-free spectroscopy to study the simplest and most fundamental of all stable atoms, hydrogen.[8] Everyone should know the Balmer spectrum series of hydrogen, in the visible and near ultraviolet, for it has been the essential key to the great advances in modern science and ultimately, technology which have so changed modern life. As the Rosetta stone unlocked the secret of Egyptian hieroglyphics, so the Balmer series opened up the laws governing atoms, and eventually molecules, liquids and solids. The spectrum looks simple and regular, and it is. Balmer was able to fit it by an equation. When Niels Bohr learned of that equation in 1913, he was able to explain it by a quantum theory. Subsequent advances in understanding that same spectrum by Heisenberg, Schrodinger and Dirac resulted in quantum mechanics, whose wide ranging consequences we are still exploring. From quantum mechanics has already come the understanding of matter and light that led not only to lasers, but to solid-state devices like transistors and integrated circuits. These devices in turn are making possible, for example, compact and powerful computers.

But the history of the hydrogen spectrum did not end in 1925. In the 1940's Lamb and Retherford used a radiofrequency method to reveal a new fine structure in the lower level of the transition that produces the red Balmer line, $H\alpha$. The discovery of this Lamb shift, along with the anomalous electron magnetic moment discovered by Kusch and Foley, led to the development of quantum electrodynamics by Feynman, Schwinger and Tomonaga.

Thus, historically the hydrogen atomic spectrum has been a testing ground where detailed theoretical predictions could be compared precisely with experiment. It is, therefore, natural to apply the new techniques of laser spectroscopy to it. Hänsch and Shahin used a d.c. discharge to excite atoms to the $n = 2$ levels, and probed the absorption by oppositely-directed saturating and probe beams from a pulsed dye laser.

The results are shown in Fig. 2. It is seen that Doppler broadening is exceptionally troublesome for hydrogen atoms which have low mass and, accordingly, high thermal velocities. Thus a perfect conventional spectrograph at room temperature can only show two peaks partly resolved, even though theory and radiofrequency studies agree on the underlying fine structure indicated. Some narrowing can be obtained by cooling the hydrogen to cryogenic temperatures,[9] but the fine structure is beautifully resolved at room temperature by saturation methods. The Lamb shift is seen, clearly resolved for the first time, in the separation of the two right-band components. (Herzberg had previously resolved the Lamb shift optically in hydrogen-like ionized helium, for which the splittings are larger.)

But the interest in observing these narrow components is not really in seeing the splittings, which have previously been determined by radiofrequency techniques, but rather to isolate individual components so that their absolute wavelengths can be determined accurately. In that way, Hänsch, Nayfeh, Lee, Curry, and Shahin[10] were able to measure the H_α absolute wavelength and so to derive a value of the Rydberg constant to an accuracy about ten times greater than had previously been possible.

Subsequently, Lee, Wallenstein, and Hänsch[11] used the saturation method to probe the second member of the Balmer series, the blue line H_β ($n = 4 \rightarrow 2$) at 486.1 nm. This line has a fine structure with smaller spacings than that of H_α, and it is more susceptible to splitting by the electric field in the discharge tube. Thus the resolution, obtained by saturation spectroscopy with the pulsed dye laser, falls considerably short of completeness (Fig. 3a). However, it is good enough to permit the first measurement of the ground-state Lamb shift in hydrogen by a comparison of the wavelength of the H_β components' centroid with that of the $1S \rightarrow 2S$ transitions. The latter was observed as a two-photon transition excited by the second harmonic of the laser and is known to be narrower than present lasers can resolve. Thus there was good reason to try to improve the resolution of H_β.

To do this, Wieman and Hänsch have recently introduced a new method which may be called "Polarization Spectroscopy,

it is like the saturation method, but the saturating beam is circularly polarized. When tuned to the center of an absorption line, the laser depletes the population of atoms oriented so as to be capable of absorbing, say, left-hand circular polarized light. Absorption of light of the complementary right-hand polarization is less affected. Thus the linearly polarized beam from the probe laser is decomposed into a circular component which is strongly absorbed, and a complementary circular component whose absorption is reduced by the effect of the saturating beam. The beam becomes elliptically polarized, and so has a component that can pass through the crossed analyzer that initially blocked the probe beam from the detector. As with the Hänsch-Bordé saturation method, if the saturating and probe beams come from opposite directions, they pick out those atoms with zero component of velocity along the beams and Doppler broadening is eliminated.

Polarization spectroscopy has a great advantage in signel-to-noise ratio. There is almost no transmission of the probe until it is depolarized by atoms pumped by the saturating beam. Thus this method can be used with fewer atoms and lower laser power.

Sometimes it is advantageous to uncross the polarizers slightly and one is then sensitive to the saturated dispersion. That also changes the polarization of the probe beam and so alters the signal reaching the detector, but now the signal can either increase or decrease. This polarized dispersion signal is, therefore, very useful for locking a laser to an asborption line.

The improved resolution of the H_β line obtained by Polarization Spectroscopy can be seen in Fig. 3b. Not only are the individual fine structure components much better resolved, but even the Stark splittings are clear enough to permit measurement of the electric field on the axis of the discharge tube. Part of the improvement comes from using a continuous-wave dye laser, which makes it easier to take advantage of the lower power levels permitted by the polarization method.

Polarization spectroscopy, whether continuous-wave or pulsed, is an important advance in techniques of laser spectroscopy. In the near future, Hänsch and Wieman will use it to improve the measurement of the hydrogen ground-state Lamb shift. Eventually, when improved lasers permit a factor of about 100 increase in accuracy, the precision of the measurement will exceed that claimed for the best quantum electrodynamic calculations and will send the theorists back to their computers. Such a large advance is clearly foreseeable.

MOLECULES

When I was a graduate student doing research under Professor M. F. Crawford at the University of Toronto, I worked on hyperfine structures in atomic spectroscopy. What little I knew about the spectra of molecules was learned from a course by H. L. Welsh, the 1974 Meggers medalist, but they did seem awfully complicated. Thus I was led to the definition of a diatomic molecule: a molecule with one atom too many!

But any molecular spectroscopist could have told me that there are very good reasons to study molecules. Their complexity ensures that there are even more unexplored areas than in atoms. Thus, there is still hope of uncovering phenomena that will require qualitatively new kinds of concepts to explain them. If atomic physics had stopped with understanding the hydrogen atom, we would not even know about electron exchange, which is surely a very fundamental concept. The concepts drawn from atomic and molecular physics are among the important guides for elementary particle physics. For instance, the ψ or J particle appears to be a sort of molecule of a charmed particle and its antiparticle.

For the laser spectroscopist, molecules have the attraction that some molecules can always be found with spectral lines coinciding with whatever laser is available. Thus it was that Hänsch and Levenson[5] first applied the method of Doppler-free saturation spectroscopy to diatomic iodine molecules. They used the several available visible laser lines from krypton and argon to probe the hyperfine structures of whatever iodine lines happened to coincide with them.

Figure 4 shows the hyperfine structure of just one of the tens of thousands of lines in the visible spectrum of the iodine molecule, I_2. Twenty-one components are expected, arising from the electric quadrupole and magnetic interactions of the iodine nuclei with the electric field gradient of the molecular electrons. All but one of them are clearly resolved, and the nuclear coupling constants can be evaluated. The enormous resolution so easily achieved here can be realized by two comparisons. On the scale that this portion is reproduced here, the visible spectrum would be about 23 km wide. The line widths of the individual components are about 6 MHz, or one part in 10^8 of the light frequency. Even that small width is largely due to pressure broadening, which Sorem was able to eliminate by working at much reduced iodine pressure and using a fluorescence intermodulation method for detecting the saturation signal.[13] Then the linewidth was limited by wavelength jitter of the available laser, to about 4 MHz. Hackel, Castleton, Kukolich, and Ezekiel have used a highly stabilized argon laser and an atomic beam to study the iodine hyperfine structure at 5145Å. They have shown that the inherent width of the iodine lines is considerably less than one MHz.[14]

Hyperfine structures of this sort have been studied for some years by the techniques of microwave spectroscopy. Iodine is an exception, as it is a symmetrical, nonpolar molecule which does not absorb microwaves, and so its hyperfine structures could not be studied previously. However, microwave spectroscopy has shown how to use the hyperfine splittings to probe electronic structures of molecules. The nuclear magnetic and quadrupole moments are fixed properties of the particular nucleus. Thus the experiments can use the nucleus as a probe to obtain information about the electron distribution in the molecule and the kind of chemical bonds involved. Levenson found that the vibrational level influenced the field gradient of the nucleus very little, even though the average distance between the iodine atom changes substantially when vibrations are strongly excited.

TECHNIQUES FOR SIMPLIFYING COMPLICATED SPECTRA

One of the difficulties in analyzing a complicated spectrum, whether atomic or molecular, is that spectral lines from unrelated levels can occur at nearly the same wavelength. Thus the spectrum can be greatly complicated by these accidental coincidences and near coincidences.

A fluorescence spectrum can be made much simpler if a laser is used to populate only one excited level. In a diatomic molecule, the emission spectrum then consists of a series of doublets or triplets, one group for each lower state vibrational quantum number. The individual lines of each group are those in which the lower-state rotational quantum number, J, differs from that of the chosen upper level by -1, 0 or +1. None of the other hundred or so J values are seen.

We could similarly label absorption lines if one could somehow ensure that only a chosen lower level is populated. However, at ordinary temperatures, very many levels are already well occupied. We might nevertheless be able to alternately increase and decrease the population of one lower level, and so to modulate just the absorption lines originating at that level. Rather than use the laser to increase the number of molecules in a given level, we can use it to decrease the population by pumping molecules out of the selected state. When those molecules are excited, they fluoresce but most of them end up in vibration levels other than the one from which they started. Thus all of the absorption lines originating on that level are weakened, until the level population is restored through collisions with other molecules.

Unfortunately, not much is known about collisional relaxation in the ground state of the particular molecule we wanted to try first, Na_2. If the relaxation is too fast, it would be difficult to change the population of any level appreciably. Therefore Feinberg, Teets, and Rubbmark[15] have made some experimental measurements of relaxation rates. Their method is shown in Fig. 6. A five-nanosecond pulse from a dye laser, pumped by a nitrogen laser, first depopulates the chosen level.

Then the absorption at that wavelength is monitored by a subsequent pulse from a second laser. The delay time between the pumping and probe pulses can be varied up to some hundreds of nanoseconds, and so the recovery of population can be monitored. By this method, the relaxation time, extrapolated to zero pressure of the argon buffer gas, was found to be around 500 nanoseconds. The cross-section for collisions with the argon atoms was determined to be 94 ± 10 Å^2 for both the (0,41) and (0,17) levels. Thus the relaxation time is long enough that a laser of modest power could modulate the population of a level in the ground electronic state of Na_2.

A lower-level-labeling experiment was done by Kaminsky, Hawkins, and Kowalski[16] even before the relaxation measurements were completed. A simplified schematic diagram of the experimental arrangement is shown in Fig. 7. Na_2 molecules were excited by a selected line from an argon ion laser, chopped mechanically at 2000 Hz. The single-mode argon laser was tuned to center of an Na_2 absorption line by the Hänsch-Bordé saturation method. Modulated absorption lines were located by a continuous-wave dye laser and their wavelengths were measured by a spectrometer.

In addition to the modulated absorption lines modulated directly from pumping out of the chosen level (Type 1 in Fig. 8), several other kinds were recognized. The initial excitation puts some population into the upper level of the transition. Any absorption from that level to still higher levels would thereby be enhanced. Also enhanced, would be the population of those levels of the ground electronic state which are populated by fluorescence from the upper level (Type 3). These levels will include some with high vibrational numbers that are initially nearly empty, and so make those states accessible for study. Finally, collisions can depopulate rotational levels close to the one originally depleted by the pumping laser, and give rise to a fourth type of modulated absorption time. The various types are distinguishable by the sign of the modulation and by the line widths.

As this work was in progress, Kusch and Hessel[17] published a preliminary analysis of the vibrational and rotational structure of the A $^1\Sigma_u^+$ state of Na_2. Their analysis resulted from measurements of thousands of lines with v values up to 20. It was complicated by the existence of a $^3\Sigma$ electronic state in the same range of energies. For such a light molecule, singlet to triplet transitions are quite forbidden and so the triplet levels are not seen directly, but they do perturb some of the observed singlet levels.

Figure 9 shows a comparison between some of the observed lines and the positions calcaulated from Kusch and Hessel's 1975 analysis. It is seen that there are deviations up to several cm^{-1} for the higher v values, although agreement is good near v = 20 where our data joins on to the region of the earlier measurements. More recently, Kusch and Hessel[18] have refined their values of the molecular constants by more completely excluding perturbed lines from their data. Their revised constants agree very well with our measurements in this region. In either case however, it is evident that the levels for the upper state vibrational quantum number, v' = 22 are strongly perturbed, as they do not at all fit on the smooth curve of the other v values.

The observed modulated lines were all narrower than the Doppler line width. Even with some power and pressure broadening, the Type 1 lines had widths around 100 MHz or about one or two parts in 10^7. This is because the pumping laser is tuned to the center of the absorption line, where it interacts with only those molecules which do not move along the direction of the laser beams. Such very narrow lines should really be measured more accurately than we were able to do with the scanning spectrometer.

DIGITAL WAVEMETER

To make quick, accurate measurements of the laser wavelength, Kowalski has developed a digital wavemeter.[19] As seen in Fig. 10, it is a two-beam, division of amplitude interferometer, related to the Michelson type but with light entering an emerging from adjacent corners. If interference fringes are counted as the corner reflector is moved through a known distance, the wavelength can be deduced. To get the accurately known distance, a beam from a standard laser is sent around the same interferometer path in the opposite direction. The two counters start at the same instant and both stop when a preset number, say one million, fringes have been counted for the standard laser. Then the dual counter displays the ratio of the counts, which is also the ratio of the wavenumbers of the two lasers.

This wavemeter has several features that make it particularly simple to adjust and use. The standard and unknown beams travel around the same path through the interferometer. It is easy to see, by the overlap of the scattered-light spots on the various surfaces, when the beam paths are coincident. The beams are distinguished by their directions, and so measurements can be made close to the wavelength of the standard, if needed. The orientation of the cube-corner reflector is uncritical. The reflector is mounted on a nearly frictionless air track and coasts freely back and forth between spring bumpers.

For higher precision, distance measurements can be made to a fraction of a fringe. Kowalski has used harmonic generation to quadruple the number of counts for a given distance of mirror travel. Thus 10^7 fringe counts of the standard wavelength laser are obtained in about 80 cm. S. A. Lee and J. Hall[20] have reported a different moving mirror wavemeter with an oscillator locked to a harmonic of the interference fringe-count frequency. Kowalski has found that the accuracy of his wavemeter is further improved by averaging a number of readings. Wavenumber intervals in the iodine hyperfine structures at several wavelengths have been reproduced with an accuracy of about 40 MHz or six parts in 10^8. Even in the simplest form, the wavemeter is accurate enough for tuning a dye laser quickly to any desired line.

POLARIZATION LABELING FOR SPECTRUM SIMPLIFICATION

Recently Teets, Feinberg, Hänsch and I have combined lower-level labeling and polarization spectroscopic techniques, so as to provide a simplified spectrum that can be seen or photographed.[21] The apparatus for polarization is shown in Fig. 11. For convenience, nitrogen-pumped dye lasers were used both for labeling by decreasing the population of a chosen level, and for probing. The pumping laser can be circularly polarized or linearly polarized. The probe is a broad-band laser giving an output spectrum essentially continuous over about 200 Angstroms.

Crossed polarizers are placed in the probe beam, before and after the absorption cell. The polarized pump laser beam, then, selectively removes molecules that happen to be oriented so as to absorb it, leaving the remainder of the molecules in that level with a complementary orientation. Thus the gas (Na_2 in these preliminary experiments) can change the polarization of the probe at the wavelengths of all absorption lines from the oriented level. Those wavelengths can then pass through the crossed analyzer and appear as bright lines in the photograph of the spectrum. In Fig. 12 the probe laser wavelengths extend on either side of the pump at about 4830Å, and cover the transitions to the low vibrational states of the B band $B^1\Pi_u \leftarrow X^1\Sigma_g^+$ of the diatomic sodium molecule. As the pump wavelength is shifted very slightly, different lower levels are polarized and the various spectra are observed. This band has been well analyzed previously, but if it were not, the B-state vibrational quantum numbers could be inferred by simply counting down until the doublets end at $v' = 0$.

It is also possible to pump a line of one band, such as the blue B band and observe in another, such as the orange-yellow A band. There we can search for perturbed levels by comparing the spacings of a number of doublets. Two of the doublets $J' = 40$, $v' = 12$ and $J' = 40$, $v' = 11$ are shown in Fig. 13. Although it is not evident in the figure, the spacing of the lower one, $v' = 11$, is 4% less than the upper one and others of that series.

The perturbed doublet shows an additional, weaker component on one side. It is believed that this is a perturbing triplet level, made visible by mixing with the nearby singlet which it perturbs. This would have been very difficult to find in the forest of lines of the ordinary absorption spectrum.

During the course of these experiments, a doublet was seen with a number of satellites (Fig. 14). This was found to be due to collisions with the buffer gas, whose pressure was higher than intended. They come from ground-state levels close to the pumped level and differing from it by 2, 4, 6 .... units of the rotational quantum number. It was to be expected that collisions can make small changes in the rotational momentum, but at first sight it seemed surprising that the molecules remain oriented well enough to be observed by the polarization technique. However, the rotational angular momentum is large enough J' = 41) so that the molecules can behave like gyroscopes whose spin direction cannot easily be changed.

The polarization methods can be used with a delayed probe pulse, or with a continuous-wave pump and probe. It should be most useful in analyzing spectra of molecules too complicated for conventional methods. It may be desirable to use an infrared laser to pump a vibrational transition to clarify the visible or ultraviolet spectra.

CONCLUSIONS AND PROSPECTS

We have seen how the ability of tunable lasers to saturate absorptions opens up many new ways of probing matter and its interaction with light. Doppler broadening from thermal motions can be eliminated and hyperfine structures revealed. Complicated absorption spectra can be simplified so that regularities and deviations caused by perturbations are made evident. The methods can be modified for small numbers of molecules by detecting changes in polarization of the transmitted light, or by fluorescence.

The scientific applications of lasers already cover an enormous range and I have been able here to look at only a small corner of one area, nonlinear spectroscopy. The discussion has been concentrated on just some of the consequences of using the intensity of laser light to alter the populations of states. I have not discussed here the use of laser light to mix quantum states and so to permit two-photon and miltiphoton spectroscopy with high resolution.[22-25] Nor has there been room to discuss coherent transient phenomena, such as quantum beats.[26]

But perhaps these few samples will indicate that as we realize more of the implications of laser light, we are rapidly extending our ability to probe the nature of light and matter. The most important discoveries by the new techniques surely lie in the future and physics, chemistry and biology will be among the sciences to benefit. Indeed selective control of chemical reactions, as for isotope separation, is approaching practicality.

We can also be sure that new understanding of light, matter and their interactions will make possible unexpected new devices. Thus when, in 1958, Townes and I were thinking about how to select the mode of oscillation in an optical maser,[27] we recognized that waves in different directions could pass through the same amplifying medium. Each would be strengthened without change of direction or wavelength, unaffected by the presence of the others. Thus we could imagine the inverse of a piece of dark glass, that would brighten an image transmitted through it. In 1970, Hänsch and Varsanyi[28] found that an organic dye, pumped by a nitrogen laser pulse, would indeed give high-resolution amplification of an image (Fig. 15).

Thus optical technology grows out of science, and science takes many of its tools and interesting problems from technology. There is very good reason to believe that with our increasingly powerful methods we are going to find surprises not only in technology but in optical science as well.

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FIGURE CAPTIONS

Fig. 1. Apparatus for Doppler-free spectroscopy by saturated absorption in an external cell.

Fig. 2. Hydrogen Balmer series and fine structure of the red line, H_α, resolved by saturation spectroscopy.

Fig. 3. Fine structure of second Balmer series line, H_β, as shown by (a) saturation spectroscopy (upper), and (b) polarization spectroscopy (lower).

Fig. 4. Apparatus for Doppler-free polarization spectroscopy.

Fig. 5. Hyperfine structure of the P(117) 21-1 B ← X transition of molecular iodine at 5682 nm (a) theoretical (b) experimental.

Fig. 6. Apparatus for measurement of lifetime for repopulation of a ground-state level.

Fig. 7. Simplified diagram of equipment for modulated-population labeling of absorption lines from a chosen lower level.

Fig. 8. The four types of modulated-population signals produced by laser saturation of an absorption line.

Fig. 9. Comparison between wavenumbers of some molecular sodium absorption lines in the A band measured by population spectroscopy and calculated from the constants of Kusch and Hessel (upper wave 1975 constants; lower 1976 revised constants).

Fig. 10. Schematic diagram of interferometer used in digital wavementer.

Fig. 11. Experimental arrangement for simplification of spectra by polarization labeling.

Fig. 12. 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.

Fig. 13. Two doublets of the A $^1\Sigma_u^+$ state of Na_2. The arrow points to a weak transition to the $^3\Pi$ level which perturbs the J' = 40 component of v' = 11.

Fig. 14. Spectrum showing collisional transfer of polarization. The circularly polarized pump laser was tuned to the B(B(4,40) ← X(0,41) transition. The microdensitometer tracing shows the superposition of collisionally induced doublets for the v' = 2 transition.

Fig. 15. Image amplifier using nitrogen-pumped dye cell. The faintly illuminated image on the slide at the left is intensified as shown at the right.

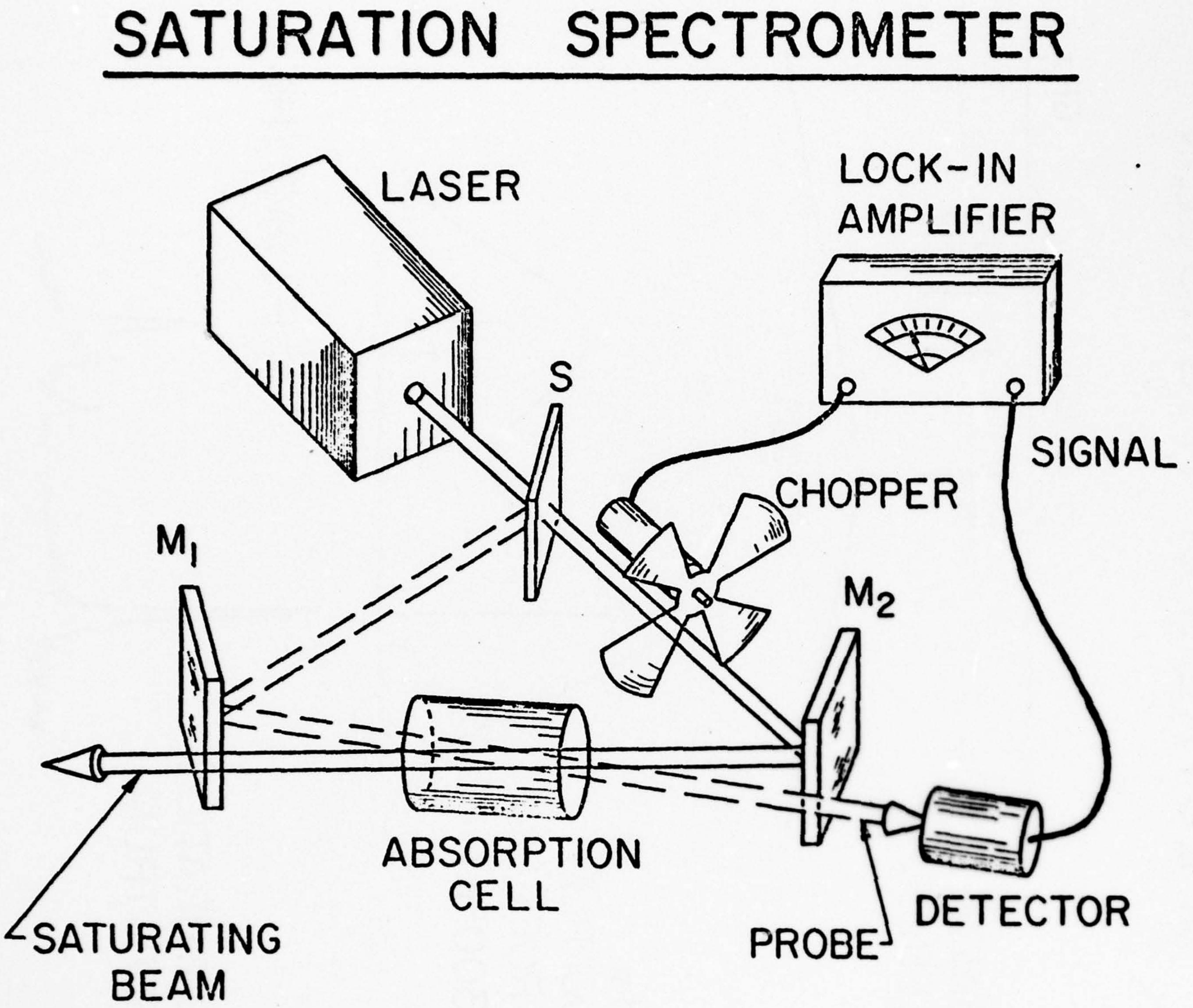
SATURATION SPECTROMETER
LASER
LOCK-IN AMPLIFIER
S
SIGNAL
CHOPPER
M_1
M_2
ABSORPTION CELL
DETECTOR
SATURATING BEAM
PROBE

Figure 1.

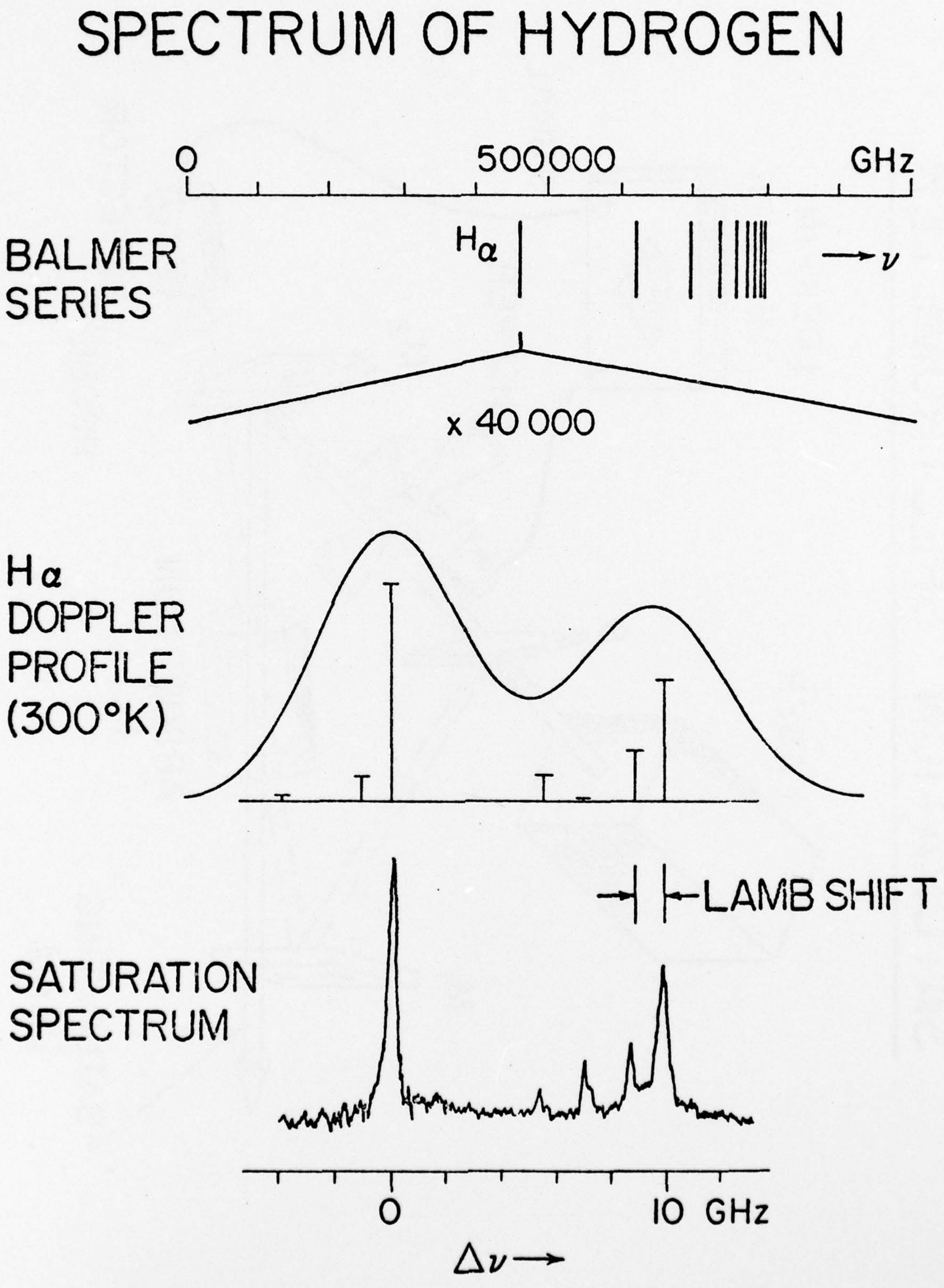
SPECTRUM OF HYDROGEN
0
500000
GHz
BALMER SERIES
Hα
→ ν
x 40 000
Hα DOPPLER PROFILE (300°K)
LAMB SHIFT
SATURATION SPECTRUM
0
10 GHz
Δν →

Figure 2.

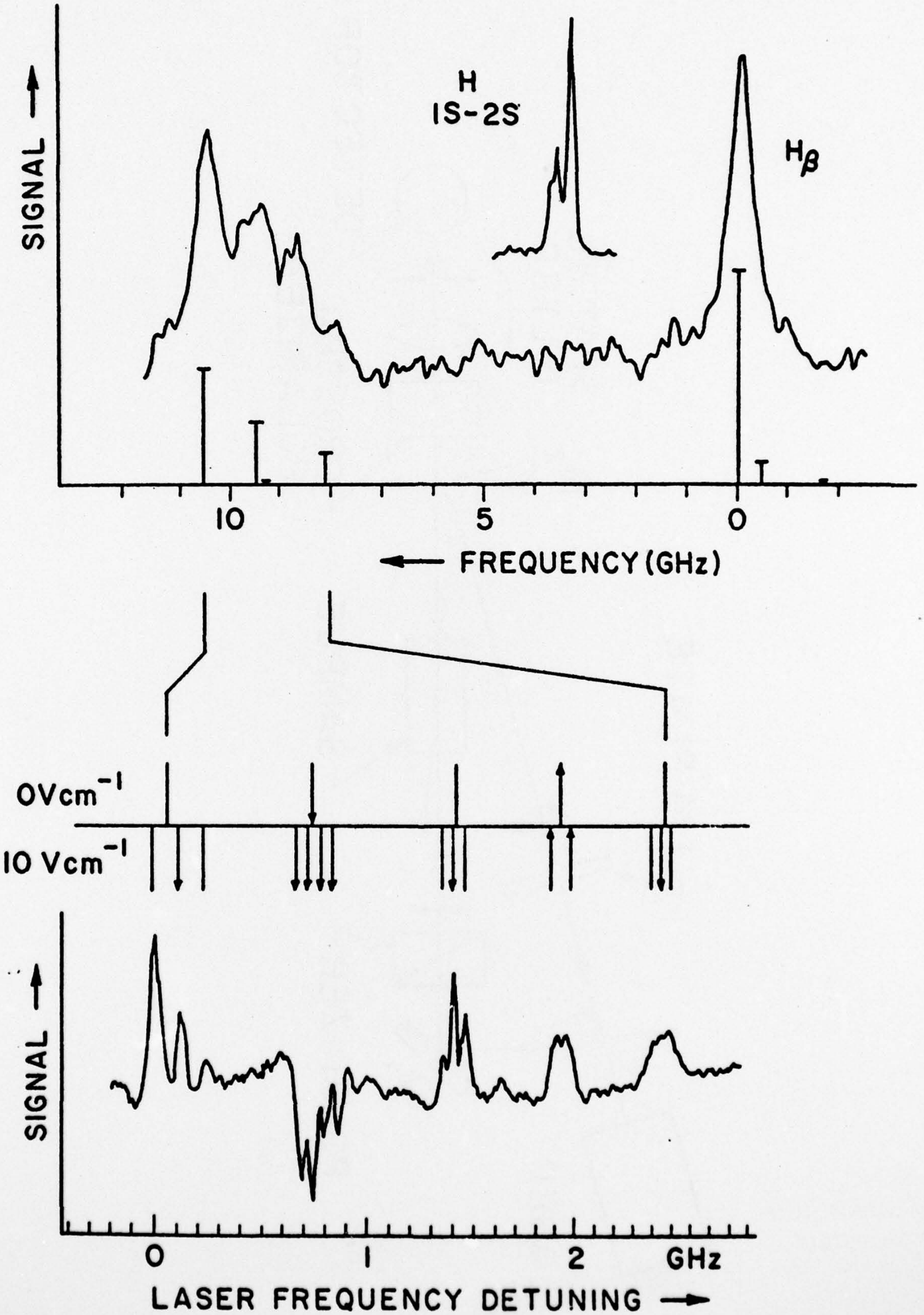
SIGNAL
H
1S-2S
Hβ
10
5
0
FREQUENCY (GHz)
0 Vcm⁻¹
10 Vcm⁻¹
SIGNAL
0
1
2
GHz
LASER FREQUENCY DETUNING

Figure 3.

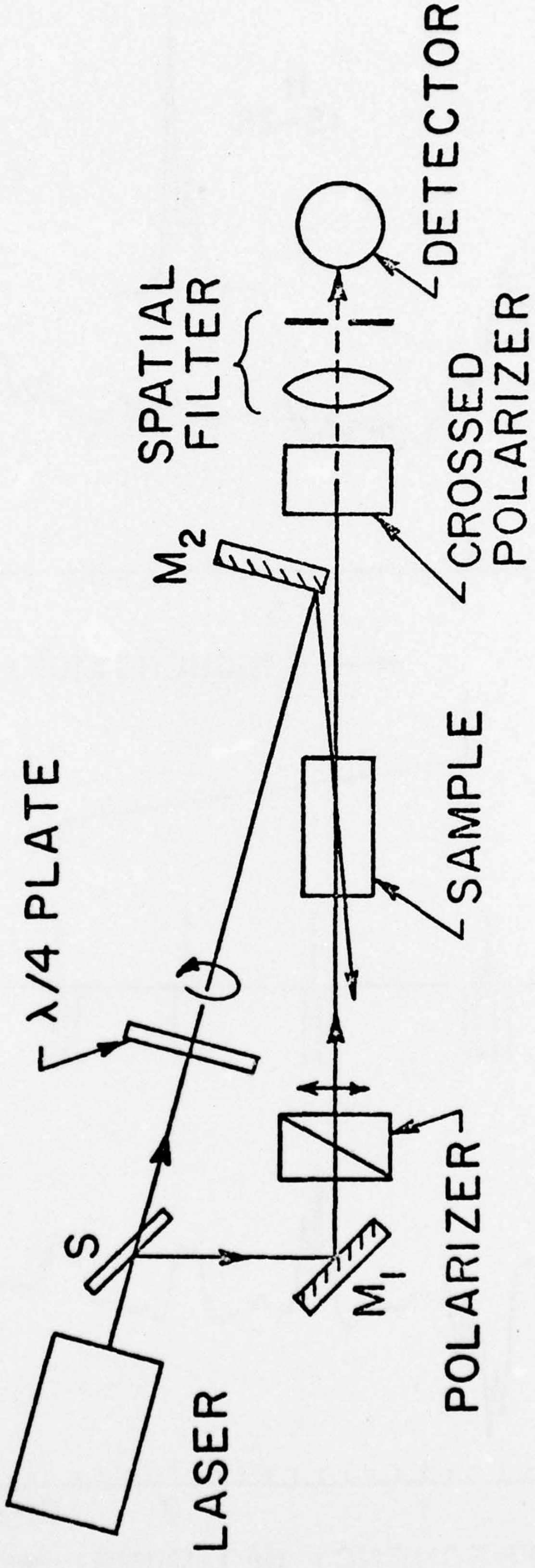
LASER
S
λ/4 PLATE
M$_1$
POLARIZER
SAMPLE
M$_2$
SPATIAL FILTER
CROSSED POLARIZER
DETECTOR

Figure 4.

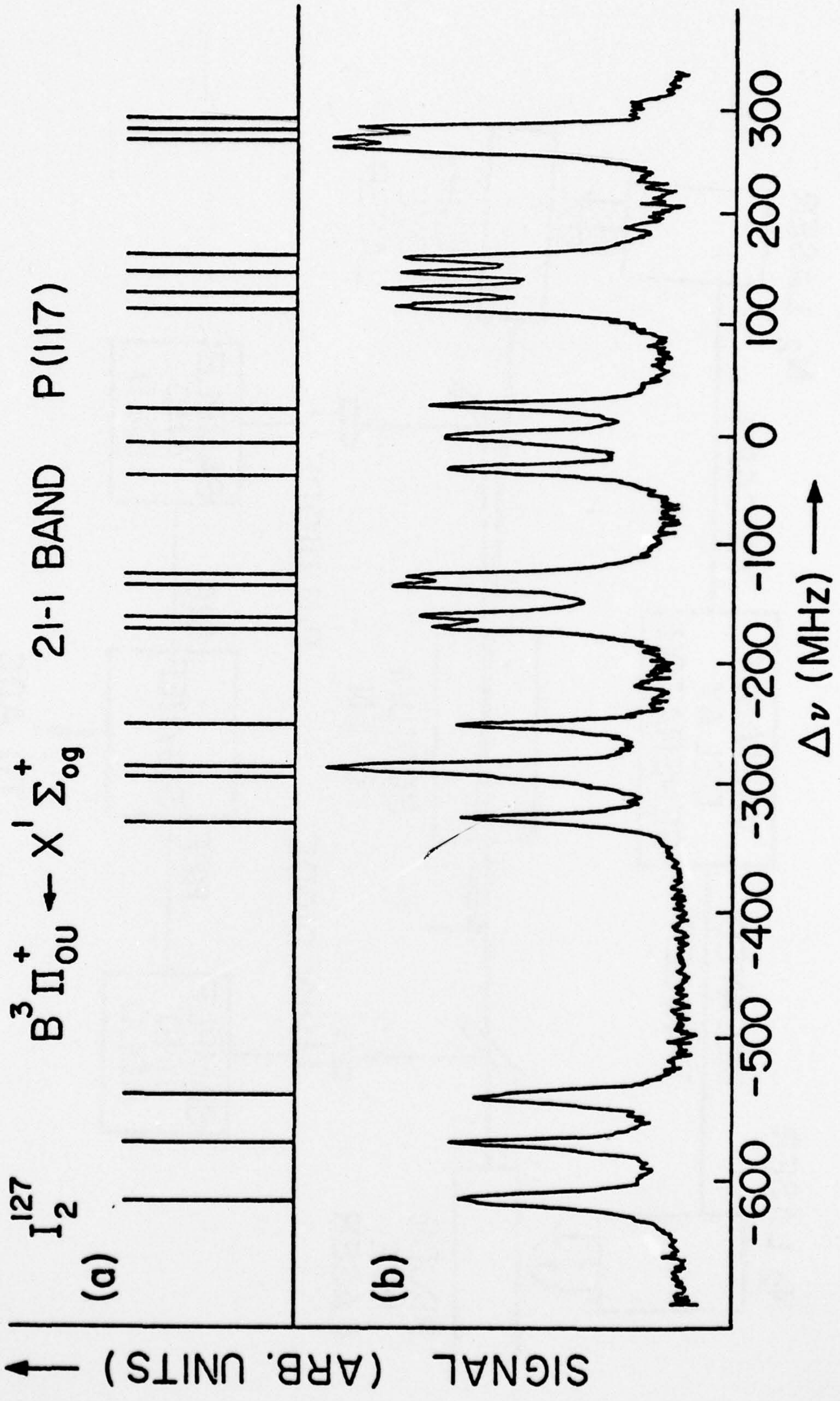
(a)
I_2^{127}
$B^3\Pi_{0u}^+ \leftarrow X^1\Sigma_{0g}^+$
21-1 BAND
P(117)
(b)
SIGNAL (ARB. UNITS) →
-600
-500
-400
-300
-200
-100
0
100
200
300
$\Delta\nu$ (MHz) →

Figure 5.

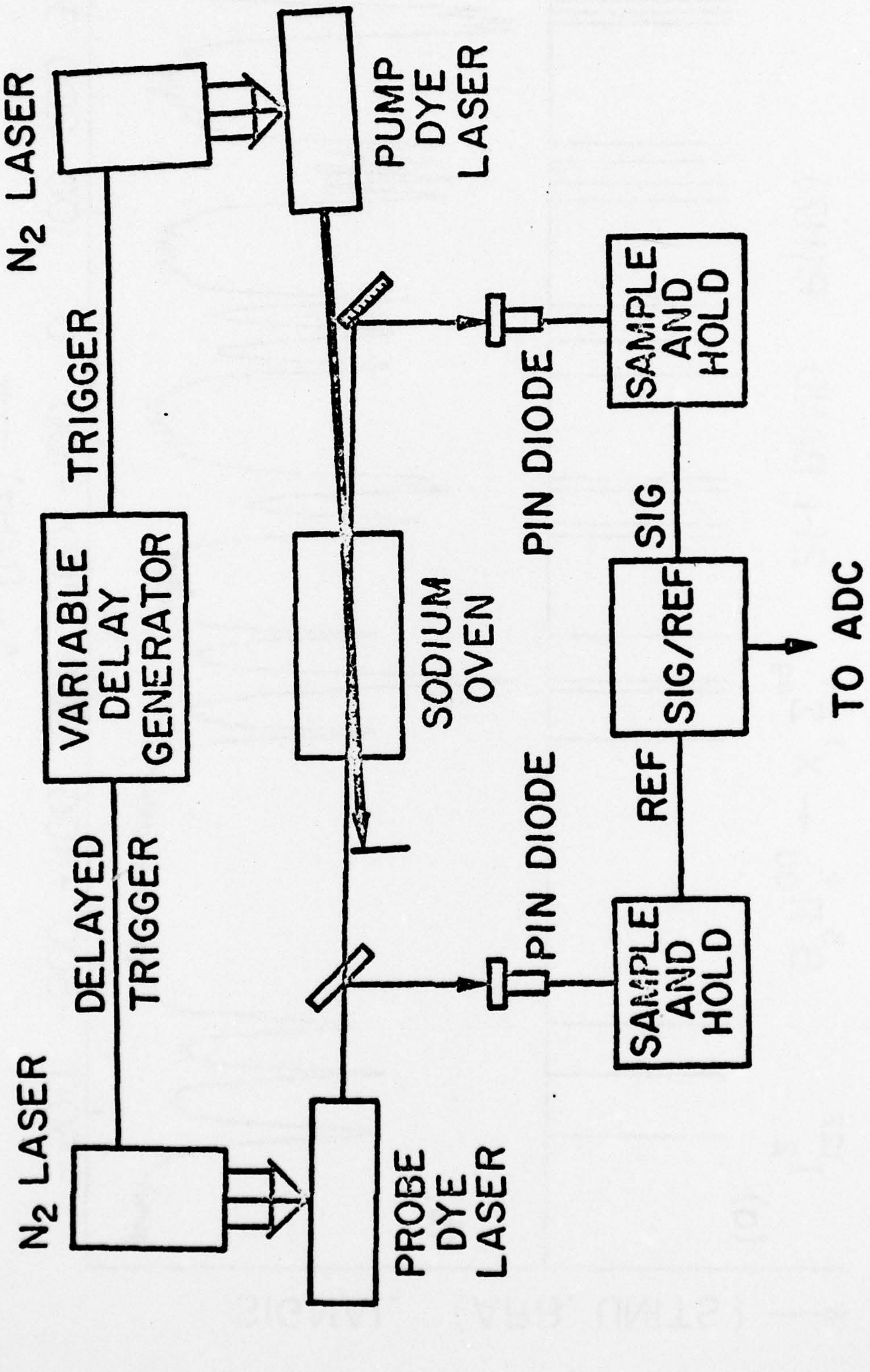
N_2 LASER
TRIGGER
VARIABLE DELAY GENERATOR
DELAYED TRIGGER
N_2 LASER
PUMP DYE LASER
SODIUM OVEN
PROBE DYE LASER
PIN DIODE
PIN DIODE
SAMPLE AND HOLD
SIG
SIG/REF
REF
SAMPLE AND HOLD
TO ADC

Figure 6.

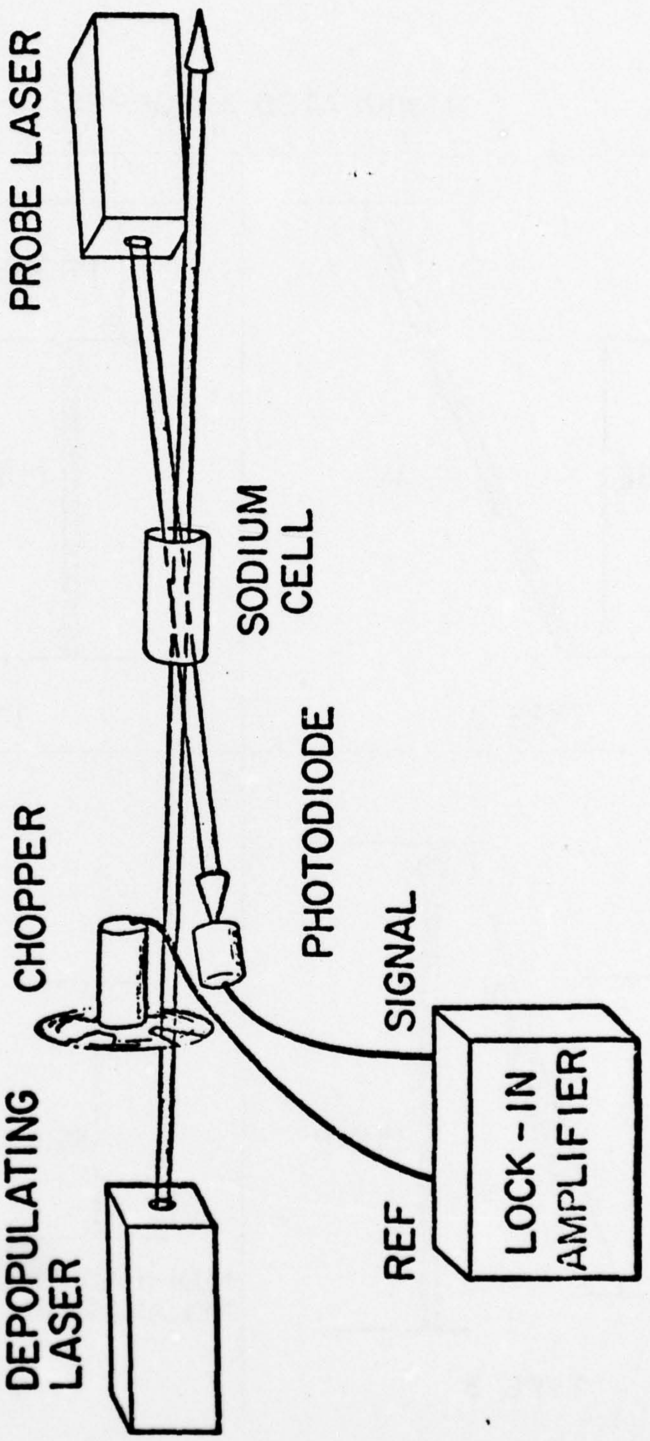
MODULATED POPULATION SPECTROSCOPY (IDEAL)

Figure 7.

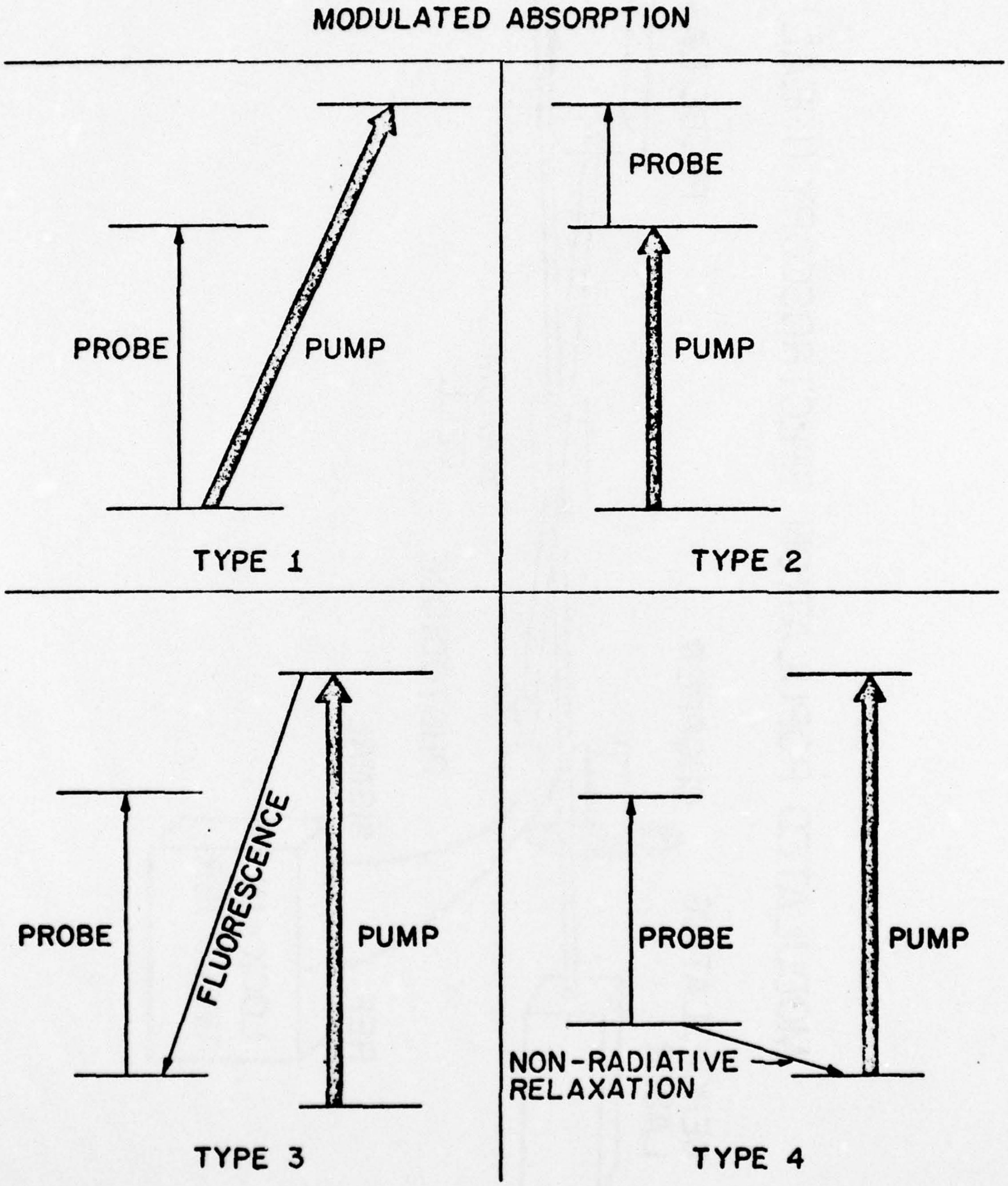
MODULATED ABSORPTION
PROBE
PUMP
TYPE 1
PROBE
PUMP
TYPE 2
PROBE
FLUORESCENCE
PUMP
TYPE 3
PROBE
PUMP
NON-RADIATIVE RELAXATION
TYPE 4

Figure 8.

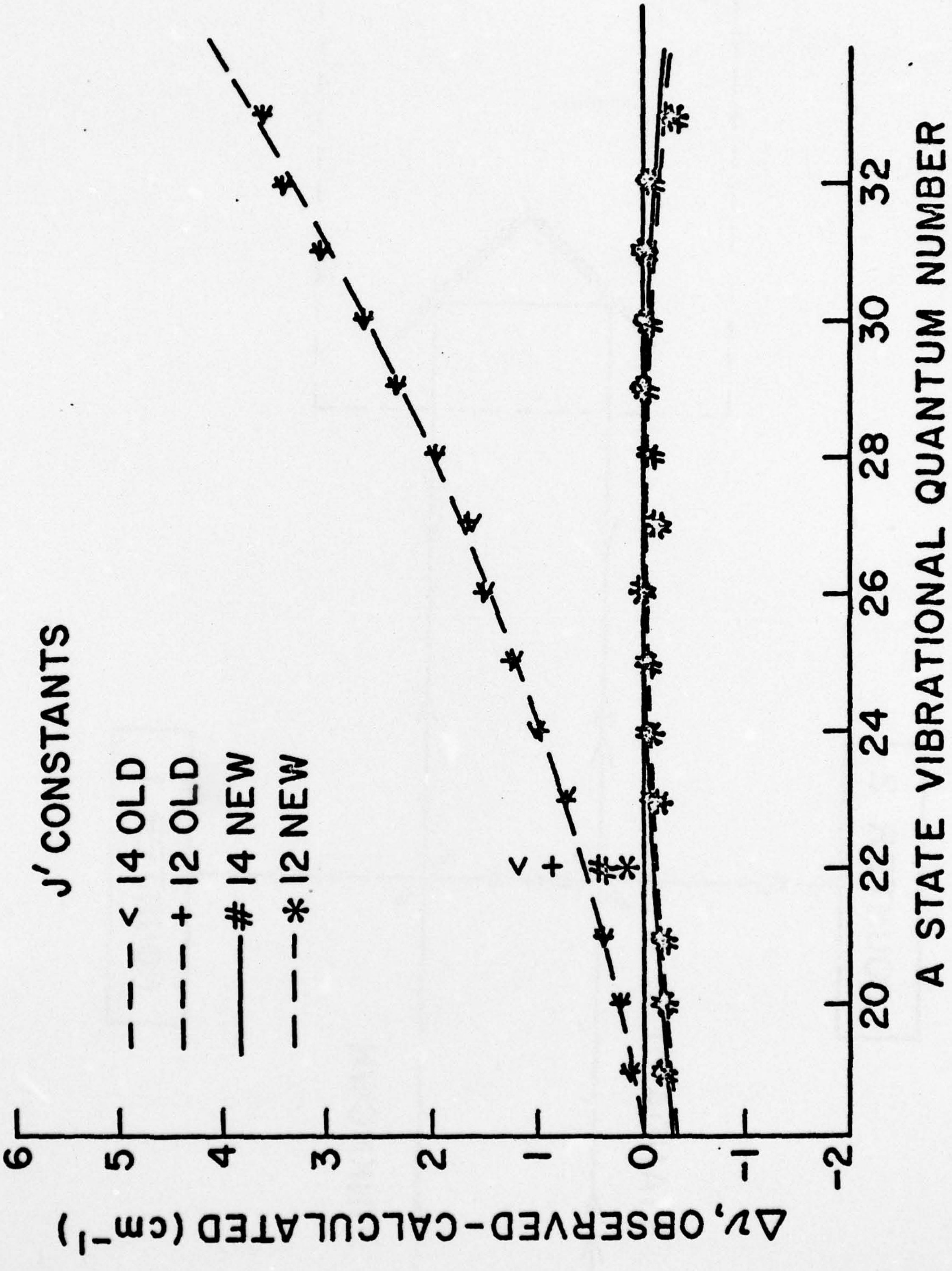
J' CONSTANTS
< 14 OLD
+ 12 OLD
# 14 NEW
* 12 NEW
Δν, OBSERVED-CALCULATED (cm⁻¹)
6
5
4
3
2
1
0
-1
-2
20
22
24
26
28
30
32
A STATE VIBRATIONAL QUANTUM NUMBER

Figure 9.

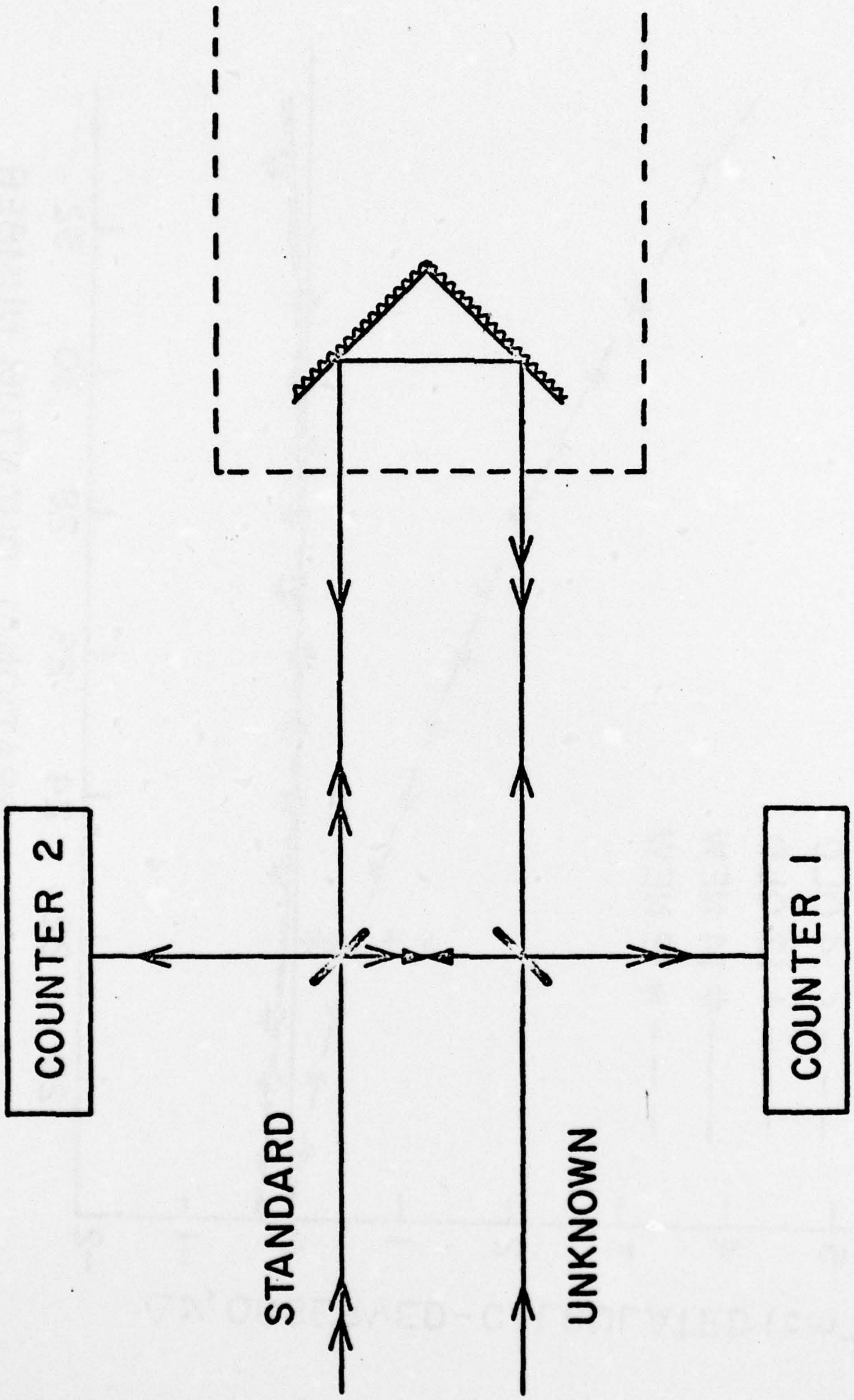

Figure 10.

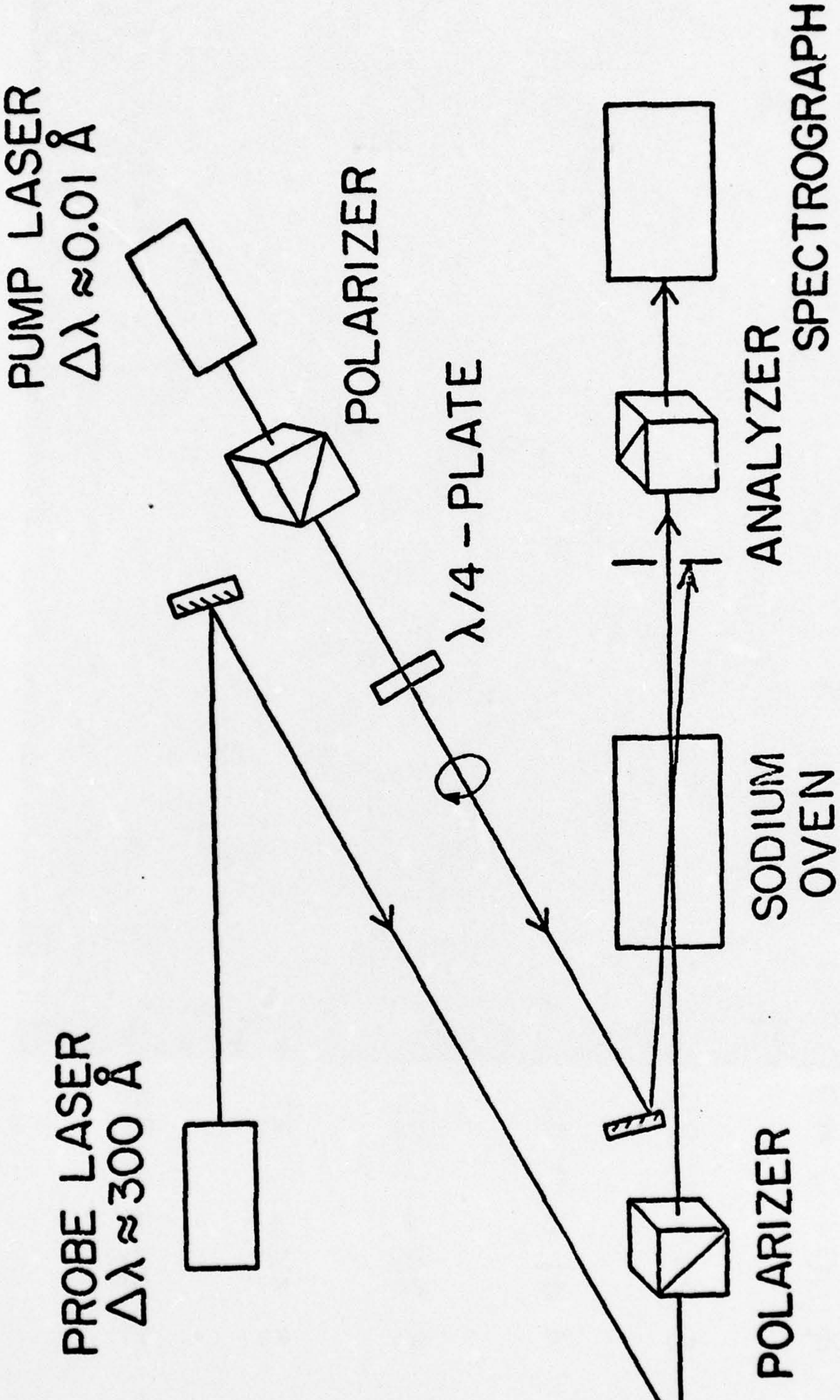
PUMP LASER
Δλ ≈ 0.01 Å
POLARIZER
λ/4 - PLATE
SODIUM OVEN
ANALYZER
SPECTROGRAPH
PROBE LASER
Δλ ≈ 300 Å
POLARIZER

Figure 11.

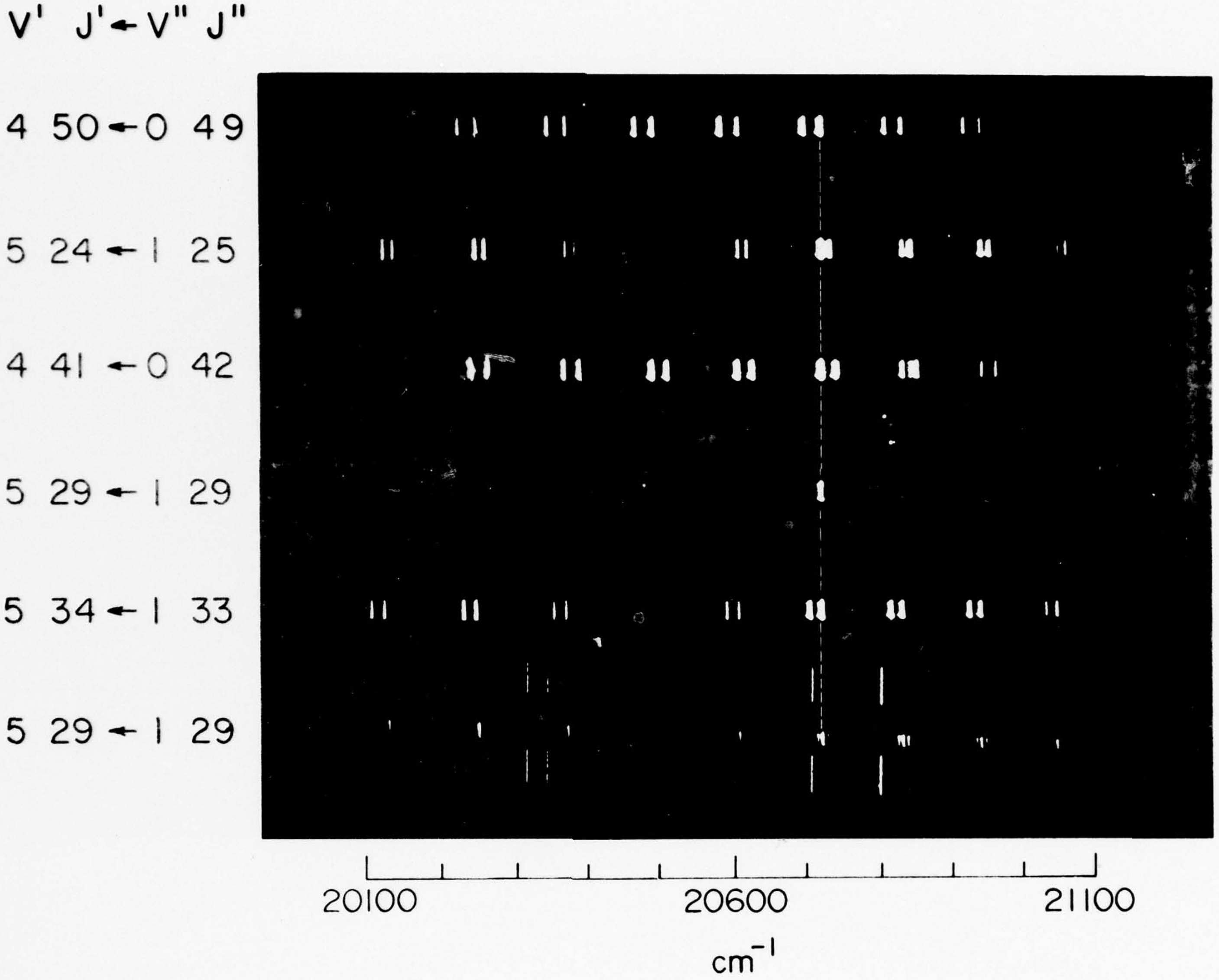
V' J' ← V" J"
4 50 ← 0 49
5 24 ← 1 25
4 41 ← 0 42
5 29 ← 1 29
5 34 ← 1 33
5 29 ← 1 29
20100
20600
21100
cm^{-1}

Figure 12

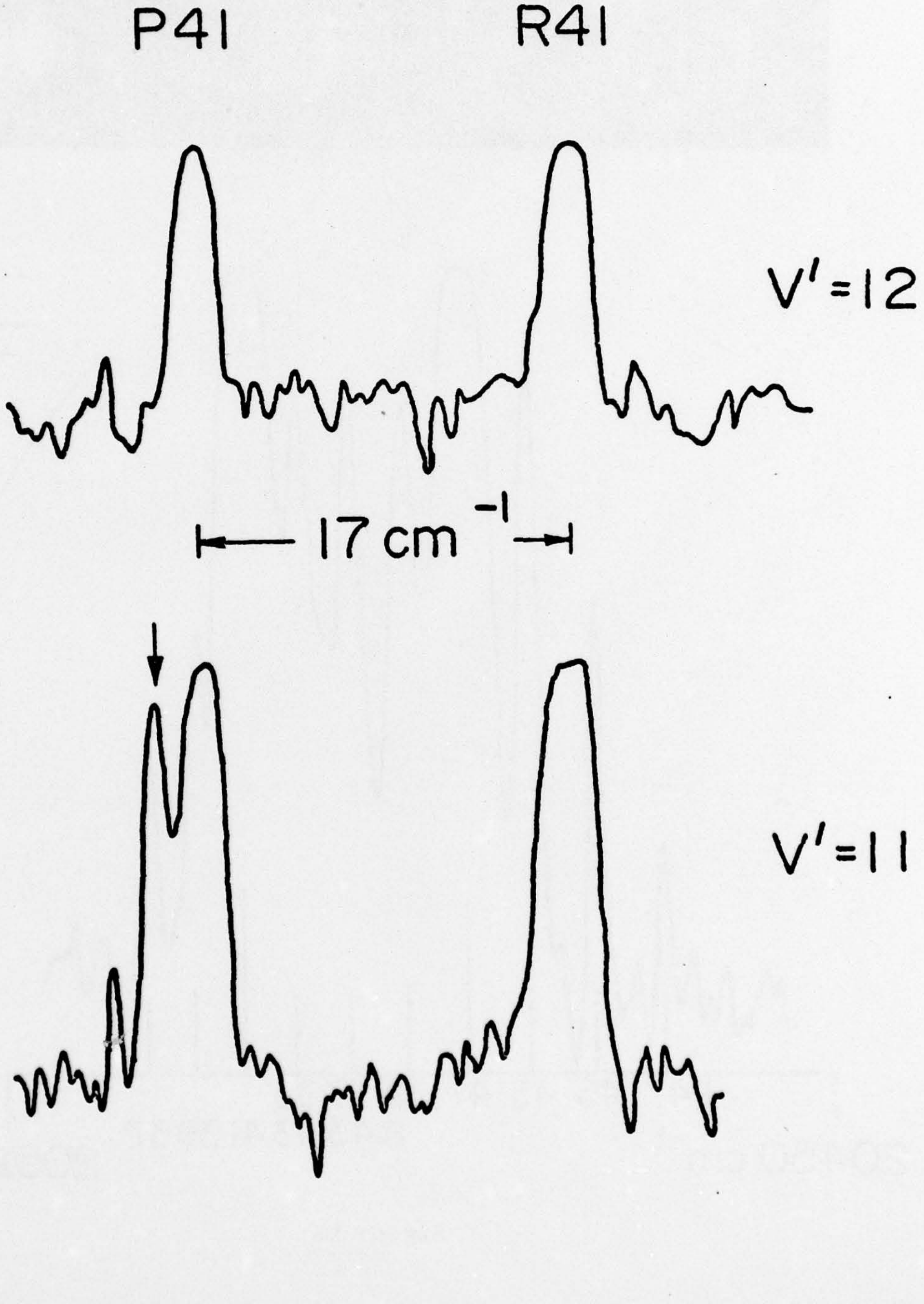

Figure 13.

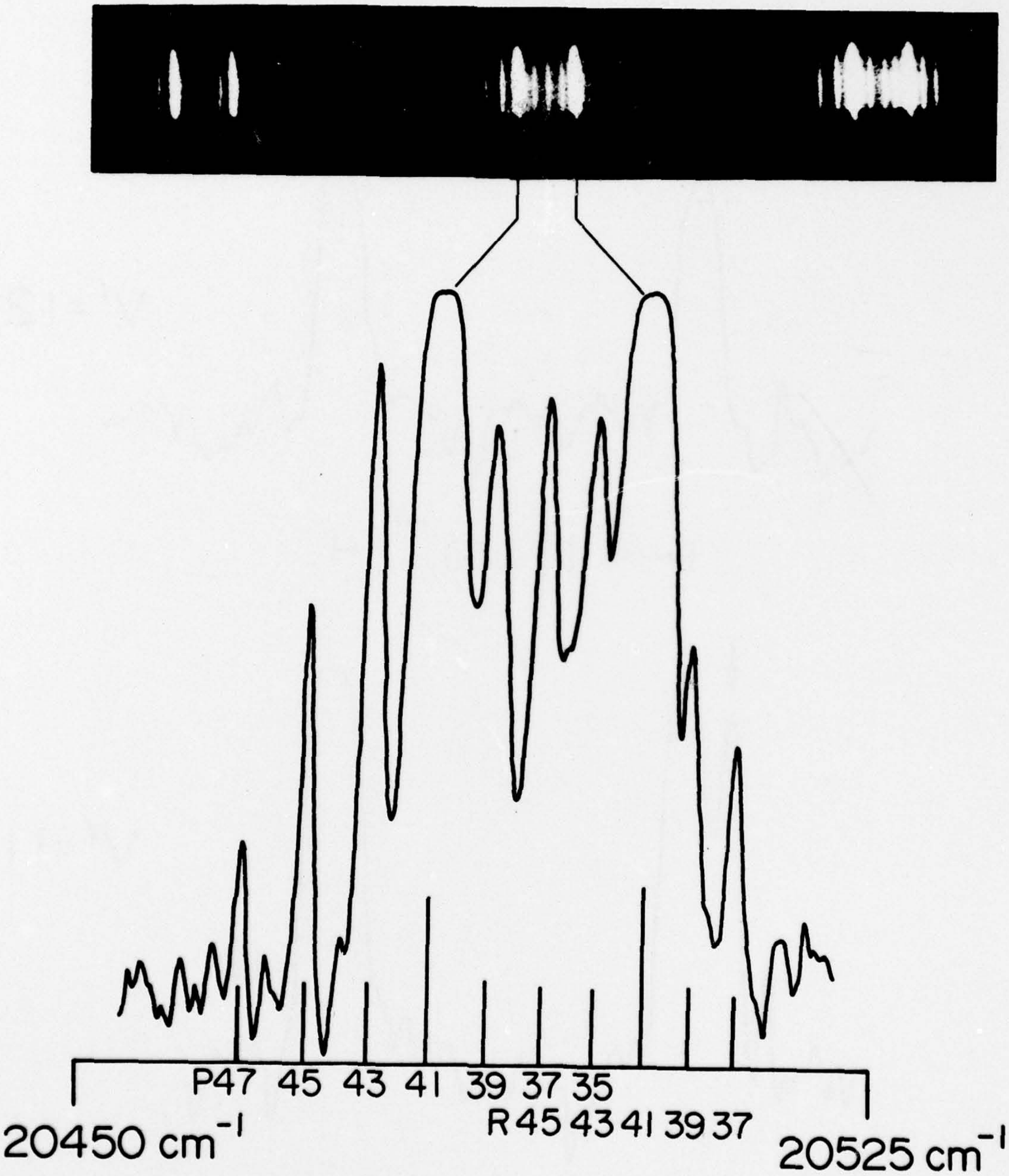

Figure 14

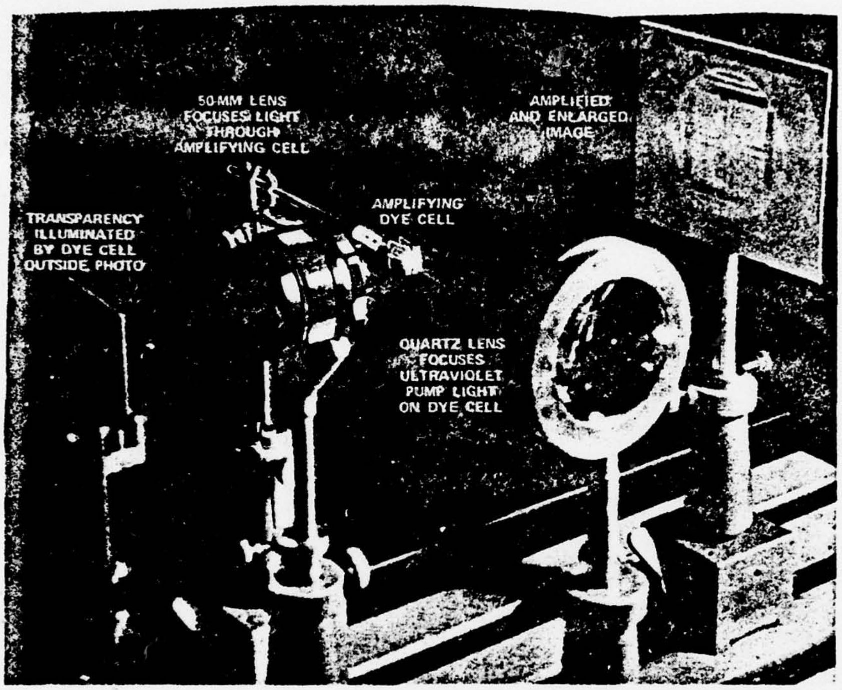
50-MM LENS FOCUSES LIGHT THROUGH AMPLIFYING CELL
AMPLIFIED AND ENLARGED IMAGE
TRANSPARENCY ILLUMINATED BY DYE CELL OUTSIDE PHOTO
AMPLIFYING DYE CELL
QUARTZ LENS FOCUSES ULTRAVIOLET PUMP LIGHT ON DYE CELL

Figure 15