

SPECTROSCOPY IN A NEW LIGHT

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by

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INTRODUCTION

Scientific spectroscopy really began in Uppsala, Sweden, where Anders Ångström in 1853 showed that some of the lines in the spectrum of an electric spark come from the metal electrodes and others from the gas between them.¹ Even earlier, Joseph Fraunhofer had charted the dark lines in the spectrum of the sun, and had measured their wavelengths.² But it was Ångström who first identified some of these lines as corresponding to bright lines emitted by particular substances in the spark. Most importantly, he showed the red line of hydrogen, now known as H α . In subsequent years, Ångström found several more visible lines from hydrogen, and measured their wavelengths accurately. When W. Huggins³ and H. W. Vogel⁴ succeeded in photographing the spectra of stars in 1880, they found that these visible lines were part of a longer series extending into the ultraviolet. J. J. Balmer⁵ in 1885 was able to reproduce the wavelengths of these lines by a formula, which we might write as

$$\frac{1}{\lambda} = \nu = \frac{R}{n^2} - \frac{R}{2^2}.$$

Balmer obtained the values of the constants from Ångström's measurements.

Five years later Johannes Rydberg⁶, without knowing of Balmer's work, developed a more general formula for the atomic spectra of alkali metals such as sodium.

$$\frac{1}{\lambda} = \nu = \frac{R}{(n-d)^2} - \text{Constant},$$

Rydberg's formula includes Balmer's as a special case where $d = 0$. The constant R is now universally known as the Rydberg constant. We know now that it measures the strength of the binding between electrons and nuclei in atoms.

It is well known that the Balmer equation for the hydrogen spectrum helped Niels Bohr to introduce a quantum theory of atoms. In the 1920s atomic and molecular spectroscopy was the principal experimental tool leading to the discoveries of the laws of quantum mechanics, from which comes most of our understanding of modern physics and chemistry.

In the 1940s when I was a graduate student at the University of Toronto,

nuclear physics seemed to be the most active branch of the subject but we had no accelerator. Therefore, I worked with two other students, Frederick M. Kelly and William M. Gray, under the direction of Professor M. F. Crawford to use high-resolution optical spectroscopy to measure nuclear properties from their effects on the spectra of atoms. The shifts and splittings of spectral lines from the interactions between electrons and nuclei were so small that they are known as hyperfine structures. To resolve them, we needed to build high resolution spectroscopic equipment. We also had to reduce the widths of the spectral lines from our light source, because broad lines cause overlapping that could completely hide much of the detail that we were seeking. When the gas density is so low that collisions could be neglected, the principal source of the line widths is the Doppler-broadening from the thermal motions of the atoms. Atoms moving toward the observer emit light that is shifted upward in frequency, while atoms moving away emit light of lower frequency than atoms at rest. Since there is a distribution of velocities, the line is broadened, with a Doppler width given by

$$\Delta\nu = \frac{2\nu}{c} \sqrt{2k N_0 \ell n 2} \sqrt{\frac{T}{M}},$$

where ν is the line frequency, k is Boltzmann's constant, N_0 is Avogadro's number, T is the absolute temperature, and M is the molecular weight.

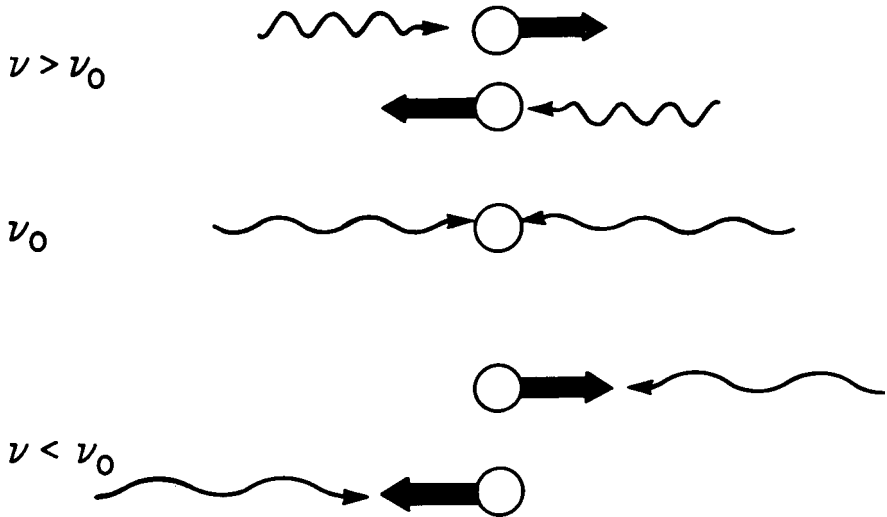
This Doppler width, as a fraction of the line frequency is of the order of \bar{v}/c , where \bar{v} is the atomic velocity and c is the velocity of light, or typically about 10^5 . We were able to reduce it by a factor of ten or so, by using a roughly collimated beam of atoms, excited by an electron beam, as had been done earlier by Meissner and Luft⁷ and by Minkowski and Bruck⁸, and by observing the emitted light from a direction perpendicular to the atomic beam. The hyperfine structures we sought could be resolved, but four hours exposure time on our photographic plates was required. It seemed that there really ought to be an easier method that would give still sharper spectral lines, and indeed a large part of our work in laser spectroscopy has been devoted to finding such methods.

LASER SPECTROSCOPY

By the time that Charles Townes and I were working to see if it was possible to make a laser⁹, in 1957 and 1958, both of us had experience in microwave spectroscopy. Thus, it was a familiar idea to us that spectra could be observed without a spectrograph, by tuning a narrowband source across the spectrum. At some wavelengths the light would be absorbed, at others it would be transmitted. This was one of the few applications we could then foresee for lasers. But each of the early lasers gave its own characteristic wavelength, depending on the material used. They could not be tuned very far, just across the width of the laser line. More tuning could be obtained sometimes by applying an external magnetic field, or by changing the temperature of a solid laser material. For instance, a ruby laser emits at 6943 Angstrom units at room

temperatures and 6934 Angstrom units at liquid nitrogen temperature of 77K. William Tiffany, Warren Moos and I used a temperature-tuned ruby laser to map out a small portion of the absorption spectrum of gaseous bromine and see how changing the laser wavelength affected the chemical reactivity of the bromine.¹⁰ We studied bromine because it had a rich spectrum with many absorption lines within the range of the available laser.

Others studied the spectra of the atoms used in a gas laser, particularly neon, and interesting phenomena were discovered. To understand them, we must note that the output wavelength of a laser is determined only roughly (within the Doppler line width) by the amplifying medium, and more precisely by the tuning of the laser resonator. By changing the spacing between the end mirrors, the laser can be tuned over the frequency range for which amplification is enough to overcome the losses. One might expect that in the center of the atomic line, where the gain is largest, the laser output will be greatest. But Willis E. Lamb, Jr. predicted, from a detailed theoretical analysis of laser principles, that there would be a dip in power output at the center of the line." It would occur because light beams travel in both directions inside the laser resonator. At the center of the line both beams stimulate the same excited atoms, those with zero velocity, as indicated in Figure 1. At any other tuning, the light waves interact with those atoms whose velocity provides just the



ν = FREQUENCY OF LIGHT

ν_0 = RESONANCE FREQUENCY OF ATOM

Fig. 1. Moving molecules interact with an approaching lower frequency wave Doppler-shifted upward in frequency, or a following higher-frequency wave shifted downward.

Doppler shift needed to bring the light into resonance with them. Thus there are two groups of atoms, with the same speed but opposite directions, which can be stimulated to provide the laser output. This "Lamb dip" at the center of the laser line was very soon observed by Bennett, Macfarlane and Lamb.¹² It was used for spectroscopy by Szoke and Javant¹³, who also showed that the narrow resonance at the dip, free from Doppler-broadening, is sensitive to broadening by collision unless the gas pressure is quite low.

Paul Lee and M. L. Skolnick¹⁴ also showed that if an absorbing gas is present inside the laser resonator, an "inverse Lamb dip" can occur, in which the laser output shows a peak at the center of the absorption line where the absorption of the molecules is saturated by the beams from both directions. The narrow, Doppler-free, optical resonances revealed by the Lamb dip and its inverse have been used for stabilizing the wavelength of lasers.

Thus by the middle of the 1960s it could be seen that, for spectroscopy, laser light possesses several advantages in addition to monochromaticity. Its intensity makes it possible to at least partially saturate absorption or stimulated emission transitions, and so to burn a narrow absorption or emission hole in a Doppler-broadened line. The directionality permits us to observe the combined effects of oppositely directed beams. Thus we could recognize the absorption from just those atoms or molecules which have zero velocity component along a chosen direction, and observe spectral details without Doppler-broadening. But at that time, we could only do so inside the resonator of some laser, and we could only work at those wavelengths where there happened to be laser lines. Later in the decade, Theodor W. Hänsch and Peter Toschek prepared the way for the subsequent advances by using the beam from a second laser on a cascade transition to probe the distribution of molecules as it was affected by saturation inside a laser.¹⁵

SATURATION SPECTROSCOPY

Laser spectroscopy became much more widely useful when, in 1970, Theodor W. Hänsch,^{16,17} and Christian Bordé¹⁸ independently introduced a method which uses these properties of laser light to give Doppler-free spectra of gases external to the laser. As shown in Figure 2, the light from the laser is divided by a partial mirror into two beams which pass through the sample in nearly opposite directions. The stronger "pump" beam is chopped at an audio frequency. When it is on, it is strong enough to partially saturate the absorption of the molecules in the region through which it passes. The probe beam then is less attenuated by its passage through the gas, and a stronger signal reaches the detector. When the chopper obstructs the pump beam, the gas absorption returns, and less of the probe's light reaches the detector. Thus the probe beam is modulated as the pump is alternately turned on and off by the chopper. However, this modulation occurs only when the two beams interact with the same molecules, and that happens only when the laser is tuned to interact with molecules at rest, or at least with zero velocity component along the direction of the beams. Any molecule moving along the beams sees one wave as shifted up

SATURATION SPECTROMETER

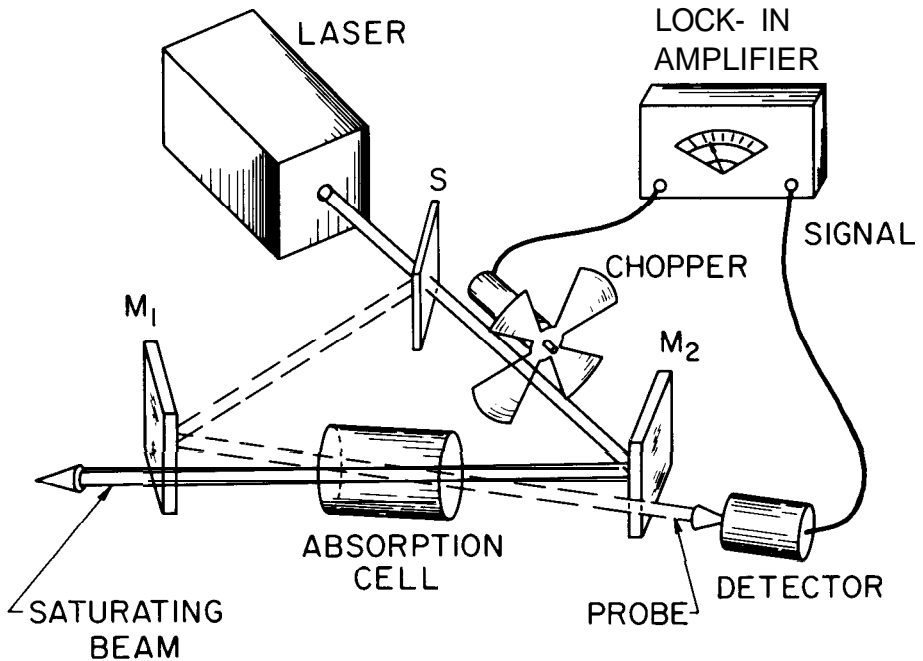


Fig. 2. Apparatus for Doppler-free spectroscopy by saturated absorption in an external cell.

in frequency and the other shifted down, and so a moving molecule cannot be simultaneously in resonance with both beams.

Hänsch and Marc Levenson applied this method first using a single-mode krypton ion laser which could be tuned over a range of about a twentieth of a reciprocal centimeter, that is, 1500 Megahertz, around the wavelengths of a few visible lines. This tuning range, although still quite limited, was enough to explore the details of several of the many lines in the dense visible absorption spectrum of the iodine molecule, I_2 . For example, Figure 3 shows the hyperfine structure of a single line in that spectrum, produced by the interaction between the molecular axial field gradient and the quadrupole moments of the two iodine nuclei. Although other workers subsequently attained considerably better resolution by more carefully stabilizing the laser wavelength, the power of the method was already a spectacular advance over what could be done before. Thus, if Figure 3 is projected on a screen two meters wide, on the same scale the visible portion of the spectrum would have a width of more than 500 kilometers! Moreover, the individual lines in the pattern, although still limited by pressure broadening and laser frequency jitter, had a width of about 6 MHz, or about one part in 10^8 . The hyperfine structures revealed, which had up to then

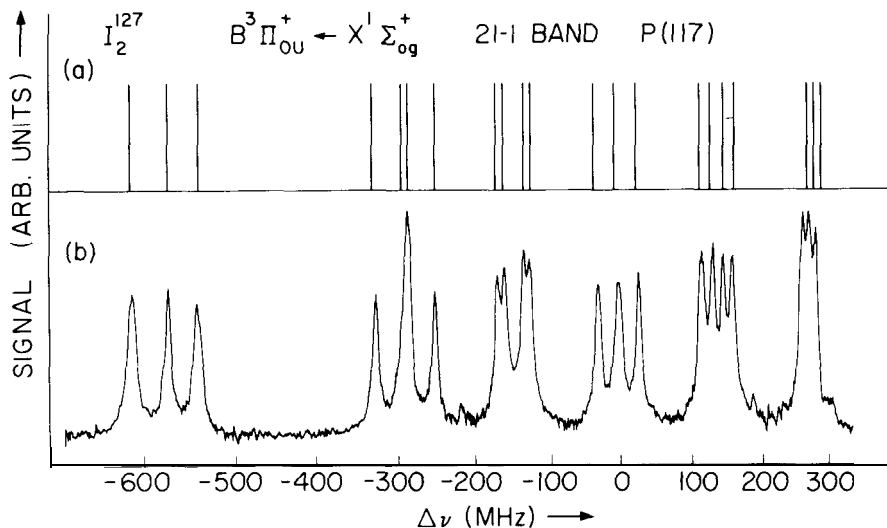


Fig. 3. Hyperfine structure of the P(117) 21-1 B \leftarrow X transition of molecular iodine at 568.2 nm (a) theoretical (b) experimental.

always been obscured by the Doppler-broadening of 600 MHz even with the best spectrographs, can be interpreted as in microwave spectroscopy to provide information about the distribution of electrons in the molecule.¹⁹

Narrow as these lines were, they were still broadened by intermolecular collisions at the operating pressure of about one torr. It was easy to reduce the vapor density by cooling the iodine cell, but then the absorption of the probe beam would be negligible whether the pump beam was on or not. However, C. Freed and Ali Javan²⁰ had shown, in some infrared spectroscopic studies, that when absorption is saturated, any fluorescence that follows from the absorption also shows a saturation. That is, the fluorescence intensity is not linearly proportional to the laser power, but levels off when the laser intensity is enough to deplete the number of molecules contributing to it. In our case the Javan-Freed method was not immediately applicable because, if the two oppositely directed beams were to work together to saturate one of the hyperfine-structure lines, it would cause only a very small change in the unresolved fluorescence in all of the components. Sorem and I, therefore, introduced a method of intermodulated fluorescence.²¹ We chopped both of the counterpropagating beams at different audio frequencies, by using two rings with different numbers of holes on the chopping wheel. Our fluorescence detector was tuned to respond to modulation at the sum of the two chopping frequencies, which arose when the stationary molecules were simultaneously excited by the two laser beams. Thus we obtained a good signal, free from Doppler-broadening, even at pressures as low as one millitorr or a thousand times less than we had been able to use with the saturated absorption method.

This is still far from the sensitivity that could ultimately be attained. When continuous wave, broadly tunable lasers became available, William M. Fairbank, Jr. and Theodor W. Hänsch tuned the laser to the orange-yellow wavelength of the sodium resonance lines. With a sodium cell designed to avoid stray light from the walls, we were able to measure the intensity of the light scattered from the sodium atoms, down to as few as a hundred atoms per cubic centimeter.²² At that density, attained when the cell was cooled to -30° C, there was on the average only one or two atoms at a time in the beam. With this method, we were able to measure the vapor density of sodium metal with a million times greater sensitivity than could previously be obtained. It was evident that laser methods could be much more sensitive than other techniques, such as radioactive methods, for detecting small amounts of suitable substances. A single atom can scatter very many light quanta without being destroyed, and so it should be possible to observe and study a single atom or molecule of a substance. Indeed, in favorable cases this sensitivity can already be achieved, by a method that uses resonant laser excitation followed by ionization.²³ The principal difficulty in making such methods broadly applicable is the lack of suitable lasers at some of the wavelengths needed, especially in the ultraviolet regions.

BROADLY TUNABLE LASERS

During the 1960s there was a rapid growth in discoveries of new laser materials and ways to excite them. Solids, liquids, and gases were made to produce laser action under optical excitation, as well as electrical discharges in gases and semiconductors. But each of them operated at its own characteristic wavelength, determined by the properties of the material, and there was no way to obtain an arbitrary wavelength even in the same spectral region. We did not at first expect to be able to produce laser operation over a continuous band of wavelengths, because we knew that the available optical amplification was inversely proportional to the width of the lasing line or band. Nevertheless, Peter Sorokin and J. R. Lankard²⁴ and, independently, Fritz Schäfer²⁵ were able to use intense flashlamps to excite laser action in organic dyes, whose emission bands could be as wide as a hundred Angstrom units or more.

A further advance came when it was realized that the high light intensity to pump broadband laser materials could be best obtained from another laser. I must admit that at first I wondered why anyone would want to compound the inefficiencies by using one laser to pump another. But when you need concentrated light for pumping, a suitable laser is a good way to get it. Thus J. A. Myer, C. L. Johnson, E. Kierstead, R. D. Sharma, and I. Itzkan²⁶ used a pulsed ultraviolet nitrogen laser to pump a tunable dye laser. As shown in Figure 4, the dye laser can consist of just a cell containing a dye in solution, an output mirror and a diffraction grating. The grating replaces the second mirror of the ordinary laser structure, and acts as a good mirror for one wavelength that changes as the grating is rotated. By now, dyes are available to give laser action at all wavelengths in the visible, extending into the near ultraviolet and

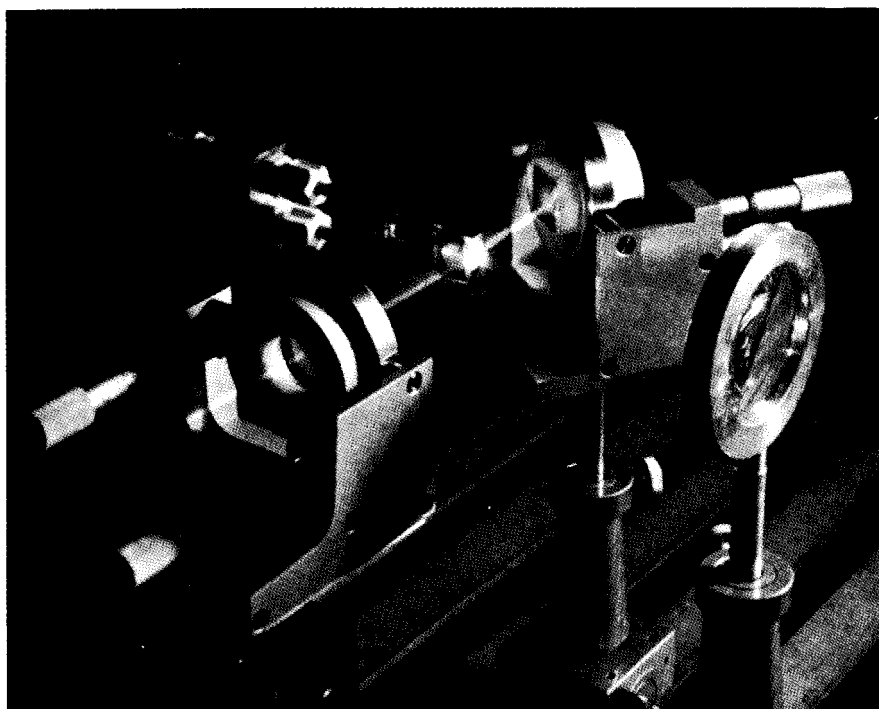


Fig. 4. Photograph of a simple pulsed dye laser, pumped by an ultraviolet beam from a nitrogen laser, and tuned by a diffraction grating.

infrared. When pumped by a nitrogen laser, the dye laser typically gives pulses of a few nanoseconds duration. The amplification is very high, so that the end mirror and the diffraction grating or other tuning element do not need to have very high reflectivity.

But such a simple dye laser of this kind typically gives an output too widely spread in wavelength to be useful for high resolution spectroscopy. Hänsch was able to obtain narrow line output by adding a telescope between the dye cell and grating. Then the light at the grating was spread over more of the rulings, and was better collimated, so that the sharpness of its tuning was improved. To get output with sub-Doppler narrowness limited only by the length of the light pulse, or about 300 Megahertz, he placed a tilted etalon in front of the grating (Figure 5).²⁷ Even more monochromatic output, with a corresponding increase in pulse length could be obtained by filtering the output through a passive resonator.

Continuous-wave dye laser operation was obtained in 1970 by Peterson, Tuccio, and Snavely,²⁸ who used an argon ion laser to excite it. The pumping laser and dye laser beams were collinear, as had been used for c.w. ruby lasers by Milton Birnbaum,²⁹ rather than in the transverse arrangement used in most earlier lasers. Refining the output of continuous-wave lasers presented difficulties because the available amplification was small, so that any tuning

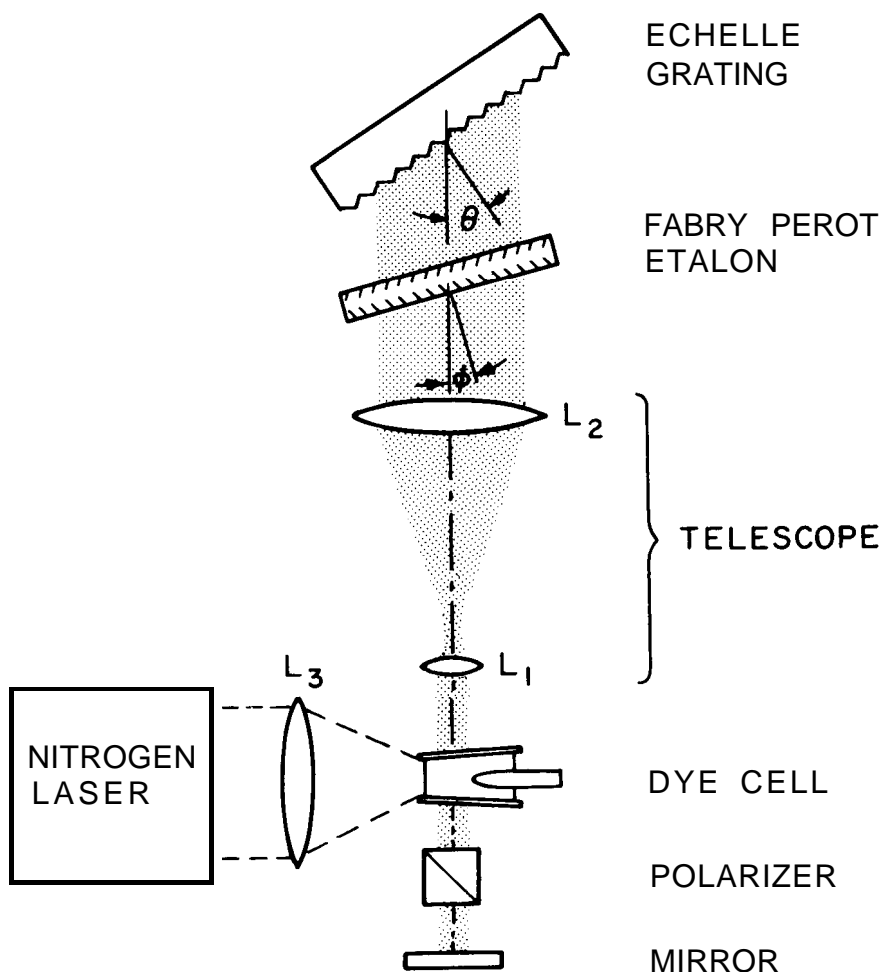


Fig. 5. Diagram of an improved dye laser, with a telescope and an etalon between the dye cell and the diffraction grating.

elements had to present low losses. But by now, extremely stable, narrowband lasers have been made, with line widths much less than one Megahertz.

Once a powerful, narrowband but broadly tunable, laser was available, it became possible to adapt the laser to the problem rather than the reverse. The methods of saturation spectroscopy could be applied to examine in detail the spectral lines of atoms simple enough to be of theoretical interest. With the pulsed dye laser, Hänsch and Issa S. Shahin first obtained Doppler-free spectra of the sodium atom's D lines at 5890 and 5896 Angstrom units, with the ground state hyperfine structure clearly resolved.³⁰ Then they applied it to study the fine structure of the red line H_{α} of atomic hydrogen.³¹ For this purpose, they constructed an electric glow discharge tube with end windows through which the two beams could pass. One beam was, as before, the saturating beam, while the other, weaker beam was the probe to detect the absorption from atoms with no velocity component along the beam direction.

HYDROGEN TERMS

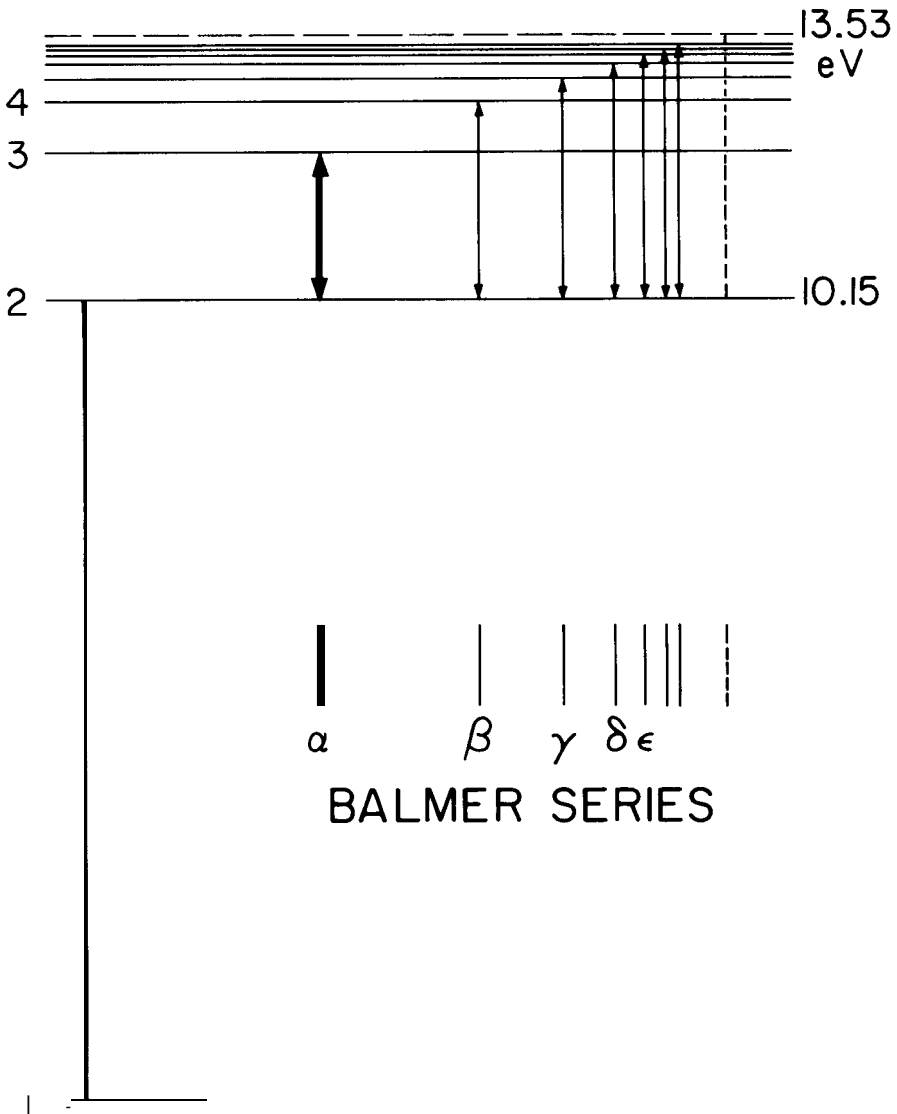


Fig. 6. Energy levels and transitions of atomic hydrogen

Figure 6 recalls the energy levels and spectral lines of the hydrogen atom according to the quantum theory of Niels Bohr. The transitions from higher levels to the level with principal quantum number, n , equal to 2 give rise to the Balmer series spectrum, drawn at the top of Figure 7. Below it is shown the fine structure of the red line, on a scale expanded by a factor of 40000, as it would be

SPECTRUM OF HYDROGEN

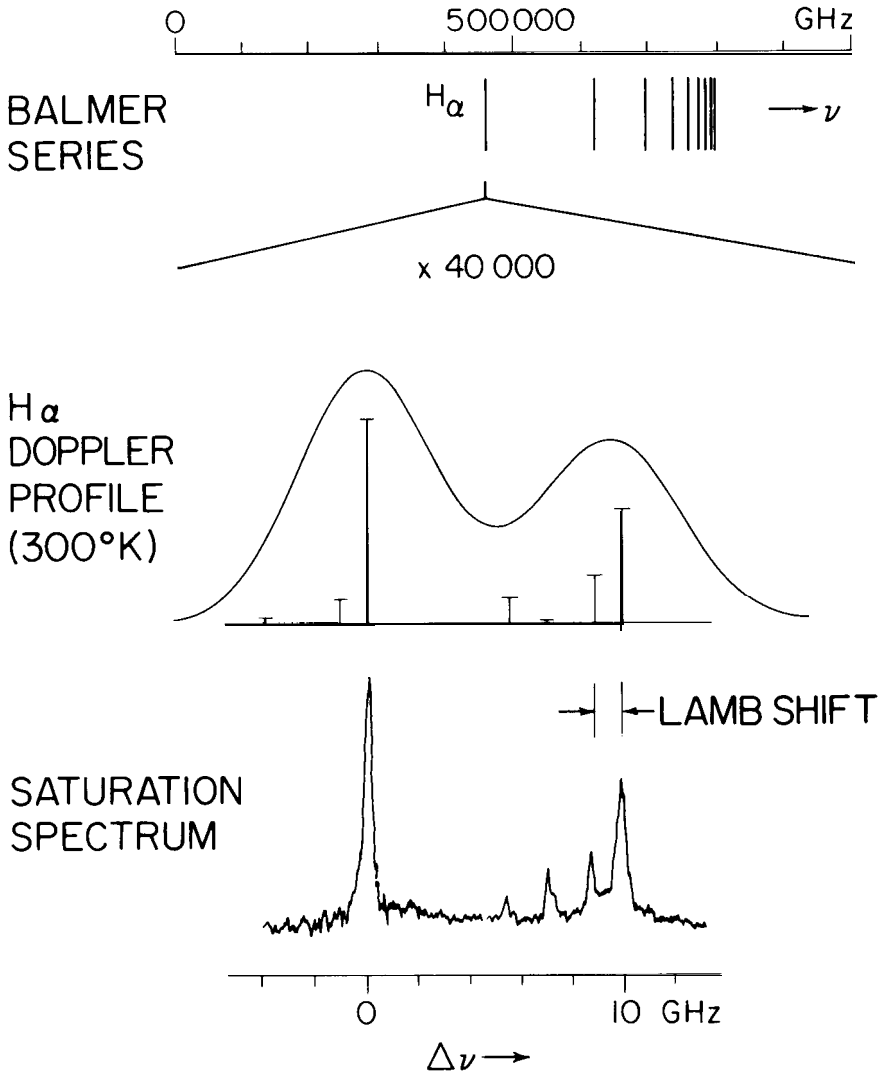


Fig. 7. Hydrogen Balmer series and fine structure of the red line H_{α} , resolved by saturation spectroscopy.

revealed by a perfect conventional spectrograph. The line is known, from theory and from radiofrequency measurements, to have the several line structure components indicated, but they would be nearly obscured by the large Doppler width. At the bottom of the Figure is shown the fine structure of this line revealed by laser saturation spectroscopy. The improvement is dramatic, and most of the details of the fine structure can be clearly seen. In particular,

the Lamb shift between the $2s_{1/2}$ and the $2p_{1/2}$ levels is clearly resolved, which had not been possible previously in hydrogen, although Gerhard Herzberg had resolved the Lamb shift in the corresponding line of ionized helium, where the shift is four times greater.³²

Microwave measurements had already given an accurate account of all of these details, and the optical resolution had little hope of improving on them. What could be done much better than before was to make an accurate determination of the wavelength of one of the components, and thereby obtain an improved value of the Rydberg constant. Of course, if the positions and relative intensities of the components are known, it is possible to compute the line shape and compare it precisely with the shape and position determined by optical spectroscopy. But the relative intensities are determined by the detailed processes of excitation and deexcitation in the gas discharge, and their uncertainty was the principal source of error in earlier measurements of the line wavelength.

Hänsch and his associates Issa S. Shahin, Munir Nayfeh, Siu Au Lee, Stephen M. Curry, Carl Wieman, John E. M. Goldsmith, and Erhard W. Weber, have refined the measurement of the wavelength of the line and thereby of the Rydberg constant, through a series of careful and innovative researches.³³ They have improved the precision by a factor of about eighty over previous work, so that the Rydberg is now one of the most accurately known of the fundamental constants. The value obtained, $R_{\infty} = 109737.3148 \pm .0010 \text{ cm}^{-1}$ is in good agreement with that obtained in a recent experiment using laser excitation of an atomic beam, by S. R. Amin, C. D. Caldwell, and W. Lichten.³⁴

In the course of these investigations, Wieman and Hänsch³⁵ found a new method to increase the sensitivity of the saturation method for avoiding Doppler-broadening. As shown in Figure 8, they used a polarized pump beam. It preferentially excites molecules with some particular orientation, leaving the remainder with a complementary orientation. The probe beam is sent through two crossed polarizers, one before and one after the sample region, so that no light reaches the detector except at the wavelengths where the light is depolarized by the oriented molecules. The saturation signal then appears as an

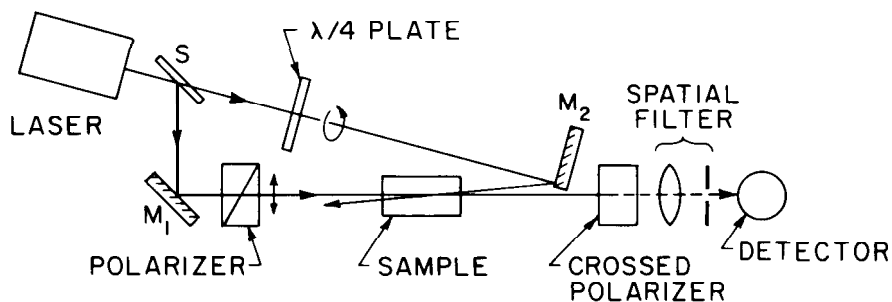


Fig. 8. Apparatus for Doppler-free polarization spectroscopy

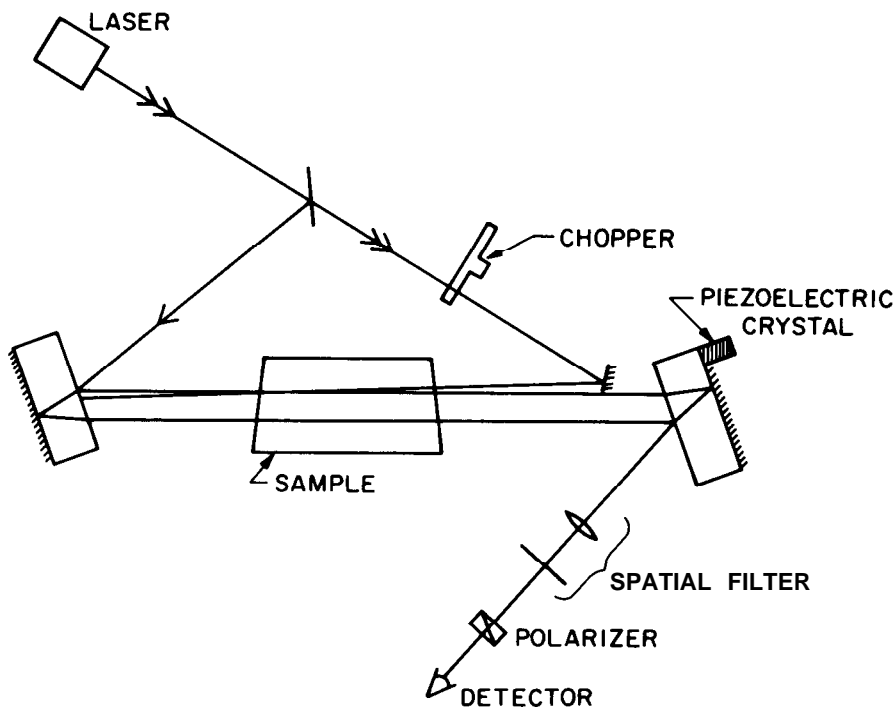


Fig. 9. Apparatus for Doppler-free saturated interference spectroscopy.

increased transmission with nearly no interfering background. Thus the noise caused by fluctuations in intensity of the probe laser is nearly eliminated, and the spectra can be observed at lower density or with lower light intensity. This method is now known as polarization spectroscopy.

Another way of balancing out the background was introduced by Frank V. Kowalski and W. T. Hill³⁶ and, independently, by R. Schieder.³⁷ They used a configuration like a Jamin interferometer, in which the probe beam is split into two parts which travel parallel paths through the sample cell, as shown in Figure 9. The beams are recombined in such a way that they cancel each other. Then when a saturating beam reduces the absorption along one of the paths, the interferometer becomes unbalanced and a Doppler-free signal is seen. In a way, polarization spectroscopy can be thought of as a special case of saturated-interference spectroscopy. The plane polarized probe wave is equivalent to two waves circularly polarized in opposite senses. They combine to produce a plane wave of the original polarization, which is stopped by the second polarizer, unless one of the two circularly polarized components experiences a different absorption or a different effective path length than the other.

SIMPLIFYING SPECTRA BY LASER LABELING

Spectra of molecules are very much more complicated than those of atoms. Even a diatomic molecule such as Na_2 has dozens of vibrational and hundreds of rotational levels for every electronic level. We have, therefore, sought systematic ways to use lasers to simplify molecular spectra so as to identify their various states. Even before lasers, something like this could be done by using a monochromatic light source, such as a filtered mercury lamp, to excite just one level, and observing the fluorescence from it to lower levels. With monochromatic, tunable lasers this can be used, for instance, to explore the vibrational and rotational structure of the ground electronic state of molecules. The upper state in this case may be said to be "labeled," since it is identified by having molecules excited to it, while neighboring states have none.

But if anything at all is known about a molecule, it is likely to be the constants of the ground electronic state, which can also be studied by microwave, infrared and Raman spectroscopy. Mark E. Kaminsky, R. Thomas Hawkins, and Frank V. Kowalski therefore inverted the process, by using a laser to pump molecules out of a chosen lower level.³⁸ All of the absorption lines originating on this chosen level were, then, weakened. If the pumping laser was chopped, the absorption lines from the labeled level were modulated at the chopping frequency. Thus when a high-resolution optical spectrometer was scanned across the spectrum, the lines from the labeled level could be recognized by their modulation, even if perturbations displaced them far from their expected position.

Almost as soon as Hänsch and Wieman introduced the method of polarization spectroscopy, it was apparent to us that it could be adapted for searching for and identifying the levels of molecules or complex atoms.³⁹ Apparatus for the polarization labeling method is shown in Figure 10. A polarized beam from a repetitively pulsed dye laser is used to pump molecules of a particular orientation from a chosen lower level, and leave the lower level with the complementary orientation. A broadband probe from a second laser is directed through two crossed polarizers, before and after the sample, and then into a

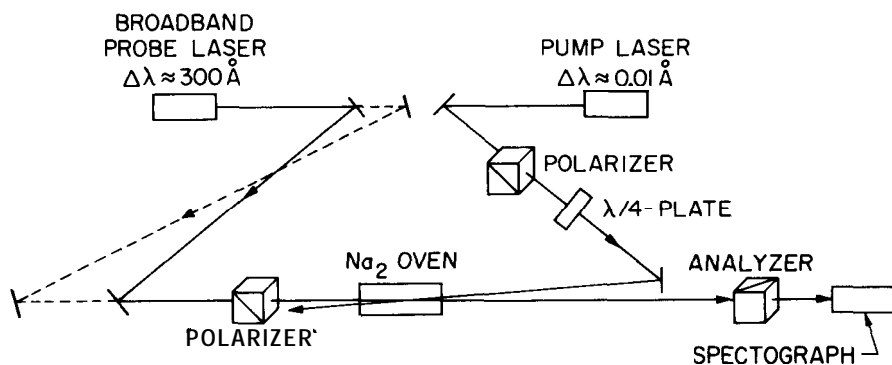


Fig. 10. Apparatus for simplifying spectra by polarization labeling.

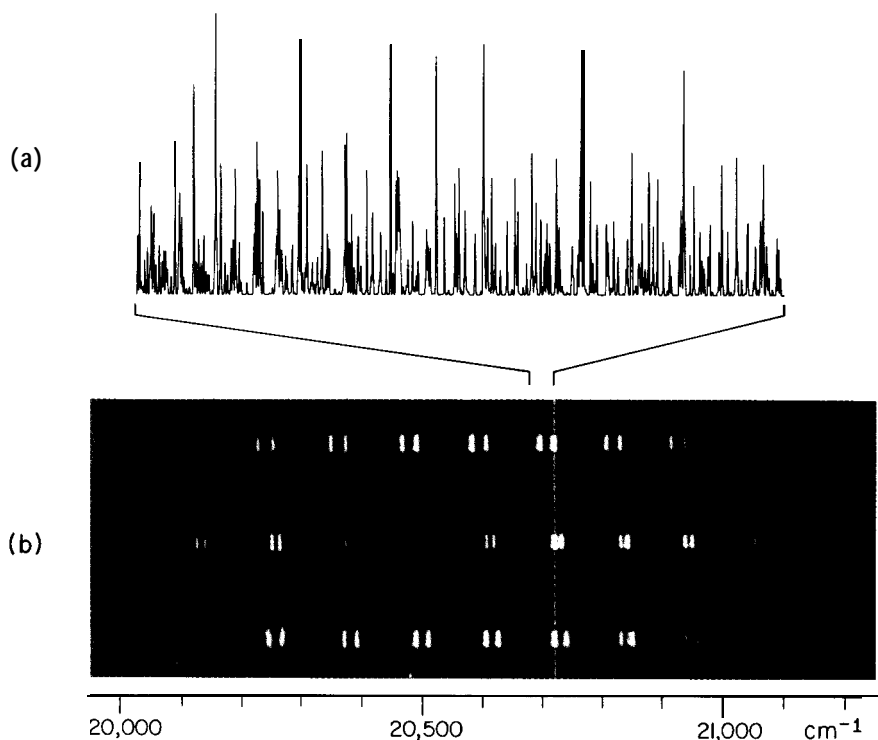


Fig. 11. A small section of the Na_2 spectrum revealed by conventional spectroscopy and by polarization labeling.

photographic spectrograph. Figure 11 shows the spectra observed by Richard Teets and Richard Feinberg,³⁹ as several neighbouring lines of N_2 are pumped. It is seen that from each labeled level, there are just two rotational lines for each vibrational level ($J' = J'' + 1$ and $J' = J'' - 1$). A small portion of the spectrum as obtained by simple absorption spectroscopy is shown for comparison. As the tuning of the pump laser is changed slightly, different groups of lines appear. For each of them, the upper state vibrational quantum number can be inferred simply by recognizing that the lines of lowest frequency end on the $v' = 0$ level of the upper electronic state.

As the molecules raised to the excited electronic level by the polarized pump laser are also oriented, the probe can record transitions from that to still higher levels. Nils W. Carlson, Antoinette J. Taylor, and Kevin M. Jones^{40, 41, 42} have identified 24 excited singlet electronic states in Na_2 by this method, whereas all previous work on this molecule had only produced information about 6 excited states. The new levels include Σ , Π , and Δ states from the electron configurations $3sns$ and $3snd$, as indicated in Figure 12. For larger values of n , these are molecular Rydberg states, with one electron far outside the core of two Na^+ ions bound mostly by the single $3s$ electron. In the Δ states the outer electron contributes something to the bonding, so that the depth of

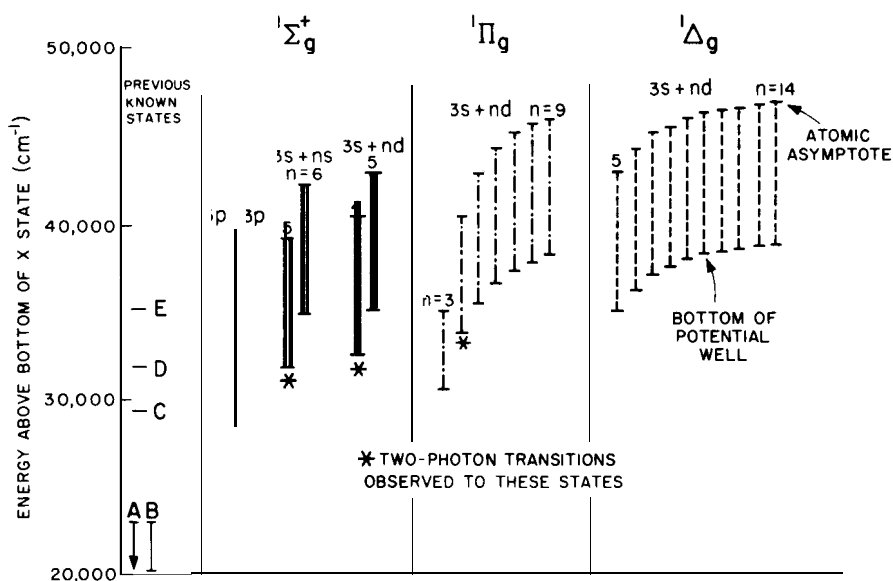


Fig. 12. Excited electronic states of Na_2 , as revealed by two-step polarization labeling

the potential well increases as n is decreased which brings the outer electron closer to the core, as is seen in Figure 13. In the Π states, the outer electron is antibonding, and so it decreases the molecular bonding when it is close to the core. Corresponding behaviors are observed for the other molecular constants, vibrational energy and bond length. Thus they can all be extrapolated to obtain good values for the constants of the ground state of the Na_2^+ ion.³⁶ This method and the several related techniques of optical-optical double resonance are making increasing contributions to the analysis of complex atomic and molecular spectra.

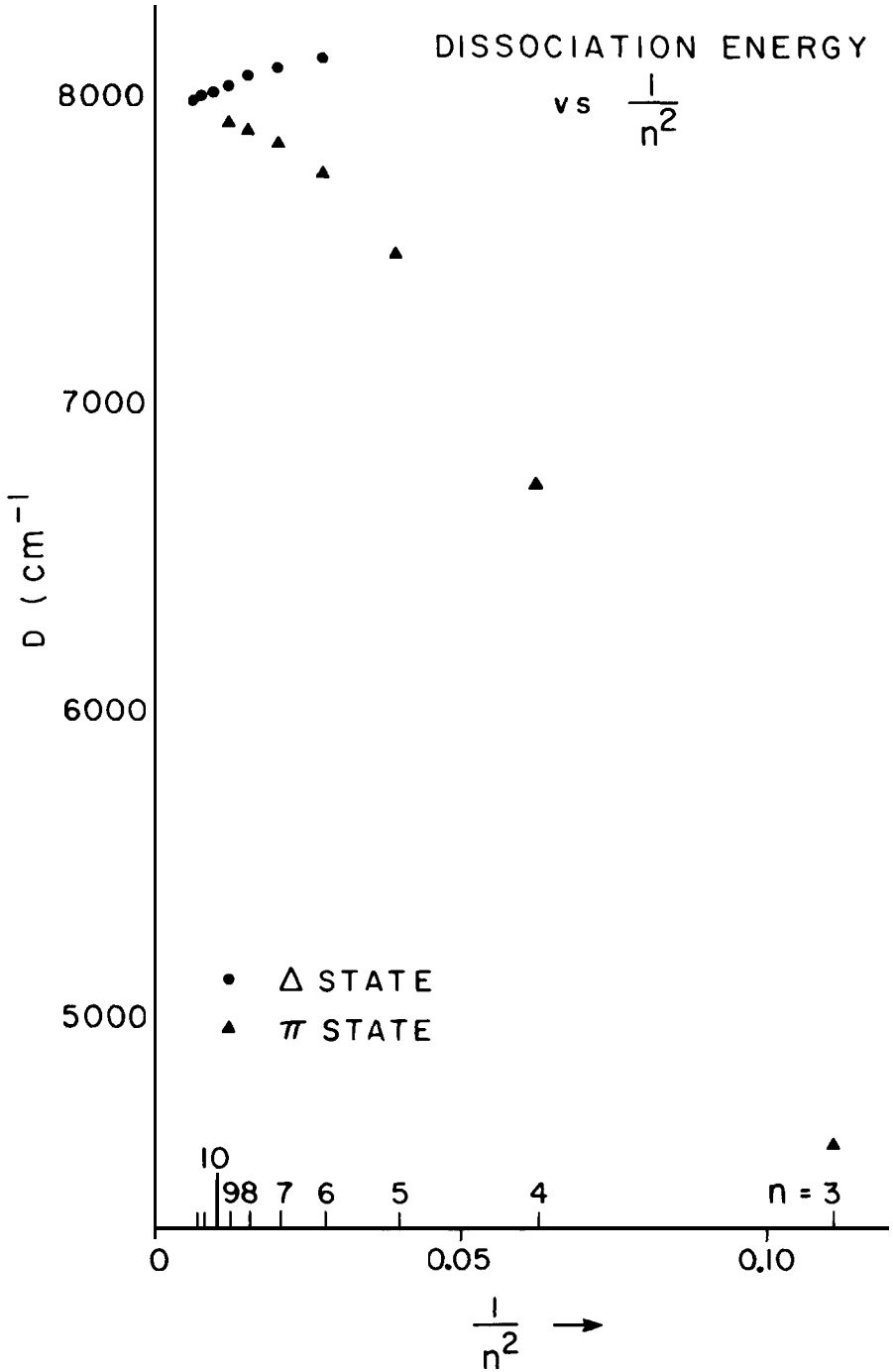


Fig. 13. Dissociation energy for Na₂ molecular Rydberg states as a function of $1/n^2$.

TWO - PHOTON SPECTROSCOPY OF Na $4d^2D$ STATE

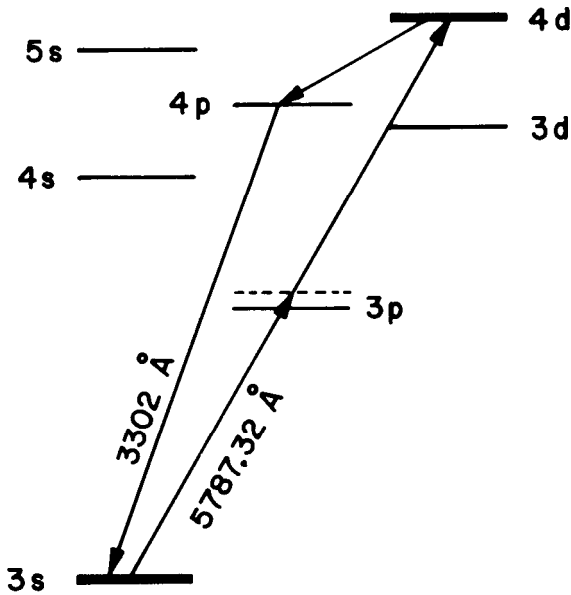


Fig. 15. Energy levels and some two-photon transitions in sodium atoms.

for the two-photon transitions. The allowed transition makes the atom more polarizable at the light frequency. Thus it enhances the two-photon absorption coefficient by a factor proportional to the inverse square of the offset, or frequency difference between the light frequency and the frequency of the allowed transition. Subsequently, R. T. Hawkins, W. T. Hill, F. V. Kowalski, and Sune Svanberg¹⁷ were able to use two lasers of different frequencies in the beams, and so to take advantage of different enhancing lines to reach a number of other levels in the sodium atom, and to measure the Stark shifts caused by an applied electric field. They used a roughly collimated atomic beam illuminated transversely by the lasers, to provide further reduction of the Doppler-broadening.

It was rather surprising, in Kenneth Harvey's early work, that some other two-photon lines were seen in the neighborhood of the expected atomic lines.⁴⁸ Since they did not exhibit the well known hyperfine structure of the sodium ground state, they could only come from molecular sodium, Na_2 (Figure 16). But that was remarkable, because the number of molecules at that temperature was very small in comparison with the number of atoms, and there would be still fewer in any individual level. Yet the molecular lines were as strong as the atomic lines. We realized that the explanation must be a more or less accidental close coincidence with some allowed, and therefore enhancing, molecular line.

DOPPLER FREE TWO PHOTON SPECTROSCOPY IN Na VAPOR

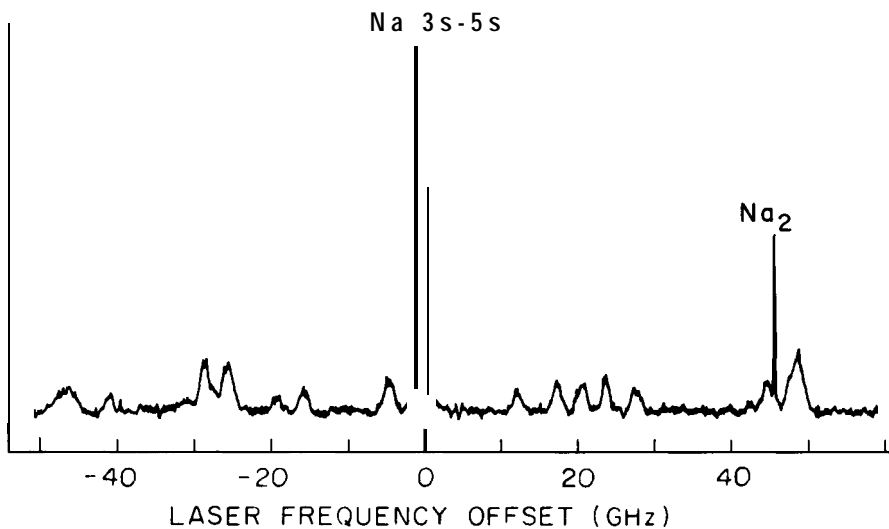


Fig. 16. Atomic and molecular two-photon lines in Na.

J. P. Woerdman⁴⁹ also observed some of these lines, and was able to identify the rotational quantum number through the nearby enhancing line of the $A \leftarrow X$ band of Na_2 . Recently Gerard P. Morgan, Hui-Rong Xia, and Guang-Yao Yan^{50,51} have found and identified a large number of these strong two-photon lines in Na_2 . The offsets from neighboring enhancing lines have been measured by simultaneous one-photon and two-photon Doppler-free spectroscopy. They are indeed small, ranging from 0.1 cm^{-1} to as little as 38 Megahertz or about $.001 \text{ cm}^{-1}$. Thus we see how it is possible to have the probability of two-photon absorption, and thus two steps of excitation, nearly as strong as that of a single step.

On the other hand, two-photon Doppler-free lines may also be observed if there is no enhancing state anywhere near, if there is enough laser intensity and sufficiently sensitive detection. Thus Hänsch, Siu Au Lee, Richard Wallenstein, and Carl Wieman^{52, 53} have observed the $1s$ to $2s$ two-photon transition in atomic hydrogen, excited by the second harmonic (2430 Angstroms) of a visible dye laser which simultaneously scans the blue H_β Balmer line. They have, thus, made an accurate comparison between the $1s$ to $2s$ interval and four times the $2s$ to $4s$ interval in hydrogen. According to the Bohr theory, the ratio of these level spacings should be exactly 4 to 1. The deviation observed is a measure of the Lamb shift in the ground $1s$ state, which is otherwise not measurable.

The $1s$ to $2s$ transition is particularly intriguing, because the lower state is stable, and the upper state is metastable so that it has a lifetime of $1/7$ second. Thus the lifetime width need to be no more than one Hertz, or a part in 10^{15} . Since we can usually locate the center of a line to one percent of the linewidth, it

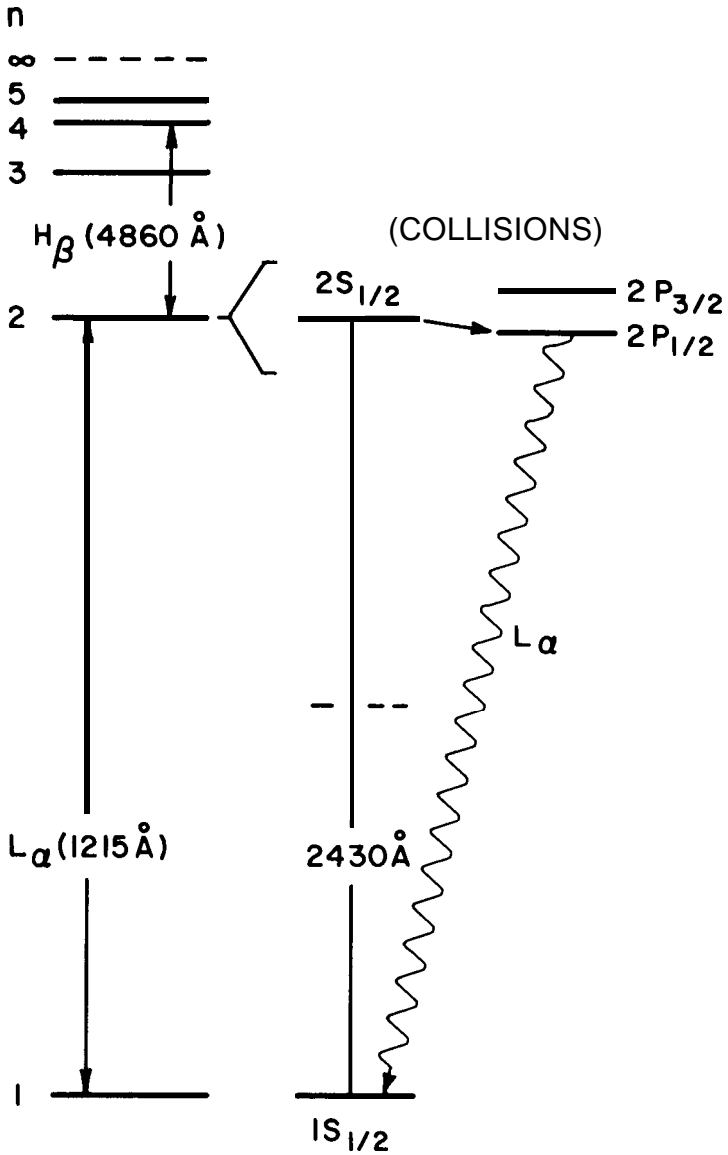


Fig. 17. Energy levels and transitions for measuring the Lamb shift of the $1s$ level of atomic hydrogen.

should be possible eventually to measure this line to one part in 10^{17} or so. But nobody measures anything to a part in 10^{17} ! Before we can hope to achieve that, such things as second order Doppler effect, transit time broadening, radiation recoil and power broadening will have to be eliminated. The challenge is great, and should occupy experimental physicists for some years.

OTHER METHODS

There is not enough room to discuss all of the laser spectroscopic methods that have interested our colleagues. Serge Haroche and Jeffrey A. Paisner have used short, broadband laser pulses to produce quantum beats in fluorescence, by exciting a coherent superposition of several hyperfine levels.⁵⁴ James E. Lawler extended the methods of optogalvanic detection of laser absorption⁵⁵ to detect Doppler-free intermodulation and two-photon lines.⁵⁶ In turn, this method has been extended by Donald R. Lyons and Guang-Yao Yan,⁵⁷ to use electrodeless radiofrequency detection of Doppler-free resonances.

Even less is it possible to begin to describe the many exciting discoveries and developments from other laboratories. Some indication of them can be obtained from the proceedings of the five biennial conferences on Laser Spectroscopy.⁵⁸ The field has had an almost explosive growth, and laser spectroscopy in some form or other extends from the submillimeter wavelengths in the far infrared to the vacuum ultraviolet and soft x-ray regions.

Thus in the powerful, directional, coherent and highly monochromatic new light of lasers, we are learning to do entirely new kinds of spectroscopy. We can resolve fine details hitherto obscured by thermal broadening, can observe and study very small numbers of atoms, and can simplify complex spectra. We can take the measure of simple atoms with a precision that is providing a real challenge to the best theoretical calculations. Our experimental capabilities have been extended so rapidly in the past few years, that there has not been time to bring them fully to bear on the interesting, fundamental problems for which they seem so well suited. But the spectroscopy with the new light is illuminating many things we could not even hope to explore previously, and we are bound to encounter further intriguing surprises.

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