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Laser Spectroscopy of Atoms and Molecules

The abundance of new laser techniques is making possible a variety of spectroscopic experiments.

Arthur L. Schawlow

Lasers have become indispensable tools for modern spectroscopy (*1*, *2*), as indeed they have for many other fields of science. Their spectral purity makes possible unprecedented resolution of fine details, and the lasers themselves provide several ways to eliminate unwanted broadening of spectral lines. They can be used to detect, measure, and study very small numbers of atoms or molecules. Complicated spectra can be simplified by laser labeling techniques. Fast transient methods can reveal relaxation rates and small splittings of energy levels. The application of these techniques is, however, limited by the availability of suitable lasers at the required wavelengths. This article surveys the kinds of things that are being done, and their present range of applicability.

Spectroscopy was one of the evident applications from the very beginning of lasers. Many of the earliest workers in the field were experienced in microwave or radio-frequency spectroscopy. They were familiar with the idea of studying spectra by tuning an oscillator through a band of frequencies. The radio wave from the oscillator was transmitted through the gas under study, and therefore its intensity decreased whenever the oscillator was tuned to a molecular absorption resonance. No spectrograph was needed, and the resolution could be as good as the frequency stability of the tunable oscillator.

Absorption Spectra with Tunable Lasers

From the beginning, it was recognized that lasers were the optical analogs of radio-frequency or microwave oscillators. Thus, they could be used similarly to probe absorption spectra over whatever frequency band they could be tuned. Unfortunately, the early lasers could be tuned only over a very small percentage of their center frequency, because these lasers were themselves based on rather narrow spectral lines. Spectroscopy was possible only for molecular lines that happened to coincide with available laser wavelengths. By now, however, there are a number of different kinds of lasers with varying degrees of tunability. Most especially, since the pioneering work of Sorokin and Lankard (*3*) and that of Schäfer, Schmidt, and Volze (*4*) in 1966, fluorescent organic dyes have been widely used as laser media whose emission bands are wide enough to provide a substantial degree of tunability. In 1970, Peterson, Tuccio, and Snavely (*5*) achieved continuous-wave dye laser operation. Since then, both continuous-wave and pulsed dye lasers have become commercially available for most of the visible and near-visible regions of the spectrum. Other kinds of devices such as parametric oscillators, semiconductor diode lasers, high-pressure optically pumped gases, spin-flip Raman lasers, and color center lasers can be used as tunable sources of coherent light, especially in the infrared.

The advent of such strong, narrowband sources in the infrared was, in itself, a revolutionary advance. Until then, all sources had been hot bodies of some kind and, therefore, the longer the wavelength, the more feeble their output. For a given source temperature, the radiated power per unit bandwidth varies as the inverse fifth power of the wavelength. Thus the power within the bandwidth of a high-resolution spectrometer would be uncomfortably small. Lasers, being nonthermal sources, have no such limitations. A highly monochromatic laser can easily give as much power as is needed for low-noise detectability with as high resolution as the spectral line widths permit. This is a useful technique even in the visible, and Fig. 1 shows a small portion of the absorption spectrum of the diatomic sodium molecule scanned by a pulsed dye laser (*6*).

Elimination of Doppler Broadening

The resolution of even an ideal spectrograph is limited by the width of the spectral lines. For free atoms or molecules at low pressures, this width is primarily caused by thermal motions. These motions are random and have a wide range of speeds. The average molecular speed is proportional to the square root of the absolute temperature and inversely proportional to the molecular weight. At room temperature, the most probable velocity ranges from 1.6×10^3 meters per second for diatomic hydrogen, a very light molecule, to 1.4×10^2 meters per second for a molecule as heavy as iodine. Because of the Doppler effect, those molecules that are moving toward the observer appear to emit or absorb light whose frequency is increased by a fraction v/c of the absorption frequency at rest, where v is the velocity of the molecule in the direction of the observer and c is the speed of light. Molecules moving away from the observer, similarly absorb or emit light that has a lower frequency (longer wavelength) than those at rest. Because of the wide range of velocities, the absorption or emission line is broadened by a fractional amount of the order of v/c. For instance, for a green line at a wavelength of 500 nanometers or frequency 6×10^{14} hertz, the line width from this thermal

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Dr. Schawlow is the J. G. Jackson and C. J. Wood Professor of Physics at Stanford University, Stanford, California 94305.

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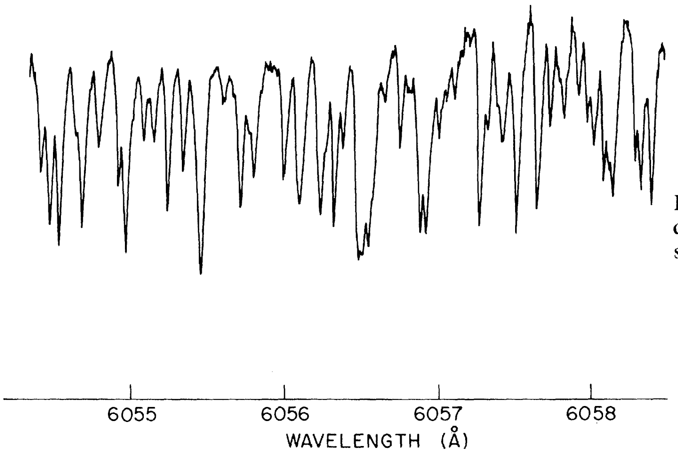


Fig. 1. A small portion of the spectrum of Na_2 scanned by a dye laser.

broadening is 460 megahertz for an iodine line and 5000 megahertz for a molecular hydrogen line. Any finer structure in the spectrum, such as might arise from the interaction between the electrons and nuclei in the molecule, would be obscured by this Doppler broadening. Yet this structure is real, and could be resolved if we could somehow observe just those molecules with a particular velocity, such as those which are neither approaching nor receding from the observer.

Many spectroscopists must have wished that they could somehow hold those molecules still, and stop them from moving around. Really all that would be needed would be to stop them from moving toward or away from the observer: transverse motions produce only the much smaller second-order Doppler shifts. Thus we can observe a molecular beam at right angles to the axis of the beam, either in absorption or emission. Although atomic and molecular beams have been used to reduce Doppler broadening for about 50 years, there are difficulties. The beam cannot be too highly directional, or it will contain very few molecules.

Moreover, if the spectrograph collects light over a finite range of angles, not all of that light can be perpendicular to the molecular beam. A laser light source can help overcome the first of these difficulties, since it can be easily bright enough to excite nearly all of the molecules in the beam, or even to excite the molecules several times over. After each excitation, the molecules will fluoresce in a short time, typically 10^{-6} to 10^{-8} second, so that a detectable amount of light can be emitted by a small number of molecules in the beam. Consequently, very small absorption coefficients of weak spectral lines can be resolved without analyzing the wavelength of the fluorescence. Moreover, the laser light can be well enough collimated to ensure that its angular spread is at least as small as that of the molecular beam.

Thus Hackel, Castleton, Kukolich, and Ezekiel have used a very monochromatic argon laser to measure the hyperfine structure of an iodine molecular line by monitoring the fluorescence from an iodine molecular beam (*7*). Their resolution and accuracy were great enough to measure not only the nuclear quadrupole, but also the nuclear magnetic octopole interaction. Pritchard, Ahmad-Bitar, and Lapatovich (*8*) used fluorescence excited by a dye laser to measure the spectrum of NaNe molecules in a molecular beam. Fine structures in NO_2 have been resolved in laser-excited molecular beam fluorescence by Bonilla, Demtröder, Paech, and Schmiedl (*9*). The process of formation of the beam by rapid expansion from an oven into a vacuum chamber results in cooling of the effective temperature of internal motions of molecules, which can be encouraged by proper design of the expansion nozzle. Thus the molecules are all in very low vibration and rotation states, so that only absorption from these lowest states can be studied. It has the advantage, however, that complicated spectra are simplified by the elimination of absorption from all but the few lowest states.

Remarkably, it has been found possible to eliminate Doppler broadening in several quite different ways by making use of the high intensity of the laser beam. In each of these, two laser beams pass through the same region of the gas, in nearly opposite directions. One beam is intense enough that it alters the properties of atoms which absorb it, so that these atoms can be recognized by the other beam. As discussed below, this either permits selection of the atoms which happen to have zero component of velocity along the beam direction, or cancelation of the effects of Doppler shifts.

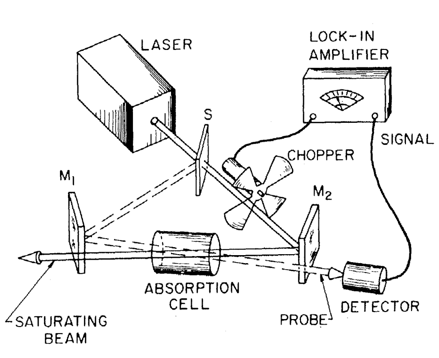


Fig. 2. Apparatus for Doppler-free spectroscopy by saturated absorption.

Saturation Spectroscopy and Related Methods

In the saturation spectroscopy technique introduced by Hänsch *et al.* (*10*) and Bordé (*11*), the two oppositely directed beams are split off from the same laser (Fig. 2). The saturating beam is periodically interrupted by a mechanical chopper. When it is on, it bleaches a path for the probe beam through the absorbing medium, and a larger intensity reaches the detector. Thus, as the saturating beam is chopped off and on, the absorption for the probe beam is alternately increased and decreased, so that the beam reaching the detector acquires an amplitude modulation at the chopping frequency. However, this occurs only if the saturating and probe beams interact with the same molecules. That is possible only if they are tuned to interact with molecules that do not move along the direction of either beam. A moving molecule would see one beam as shifted up in frequency and the other shifted down, and so it could not be simultaneously resonant to both. Consequently, in this method, only the spectrum of molecules which are standing still, or at most moving perpendicular to the beam, is recorded, and therefore the first-order Doppler effect is eliminated.

Figure 3 shows the hyperfine structure of a single line of the iodine molecule resolved in Doppler-free saturation spectroscopy by Hänsch, Levenson, and Schawlow (*10*). The 21 hyperfine components, arising from the interaction between the molecular electrons and the iodine nuclei, are almost completely resolved. Individual lines have a width of about 6 MHz, or one part in 10^8, and even that small width is largely caused by pressure broadening and frequency jitter of the available laser. On the scale of Fig. 3, the visible portion of the spectrum would have a width of about 25 kilometers.

Hänsch and Shahin (*12*) applied the

saturation method to the red Balmer line, H$_\alpha$, of atomic hydrogen. Doppler broadening is especially large in hydrogen, as it is the lightest of all stable atoms. With the best conventional spectrographs, only two components could be resolved, but the laser method clearly separates the major fine structure components (Fig. 4). They were thus able to make an improved measurement of the absolute wavelength of one of these components, so that subsequently a value was derived for the Rydberg constant good to about one or two parts in 10^8 (*13*).

The saturation method is being widely used to eliminate Doppler broadening of spectral lines. However, if there are few molecules in the absorbing state, as there might be for rare species, for excited states with small population, or for any state in a gas at low pressure, there is little absorption available to modulate by saturation. In those cases, it may still be possible to use saturation to tell when both beams are tuned to resonate with stationary atoms, by observing the fluorescence. It was noted by Freed and Javan (*14*) that, when the absorption is saturated, the fluorescence produced by the absorption also must saturate. Sorem and Schawlow (*15*) were able to detect the saturated absorption of molecular iodine at a pressure of 1 millitorr—a thousand times lower than in the saturated absorption experiments of Hänsch, Levenson, and Schawlow (*10*)—by chopping the two antiparallel laser beams at different frequencies f_1 and f_2. The detector was arranged to observe only fluorescent light modulated at the sum frequency $f_1 + f_2$, which could be produced only when the two beams interacted with the same molecules.

In Doppler-free spectroscopy by saturated absorption, the extent of saturation, and hence the degree of modulation of the probe, must be kept small to avoid power broadening. Small fluctuations in the beam intensity may mask the signal, especially if the absorption line is weak or there are few absorbing molecules. To some extent, laser intensity variations can be reduced by subtracting the probe intensity from that of a second probe which has not passed through the saturated region. Kowalski *et al.* have shown that the two probes can be balanced in both amplitude and phase by using the arrangement shown in Fig. 5, which is a structure like the Jamin interferometer (*16*). The two probe beams pass through the gas sample side by side. If they are adjusted to cancel in amplitude and phase, the signal at the detector will increase from nearly zero when the saturating beam upsets the balance. Thus the signal-to-background ratio is greatly improved in this saturated interference method. It is also possible to continuously adjust for best phase balance as the laser is scanned, so that only amplitude changes produce a signal. The change in intensity at the detector is then proportional to the square of the change in absorption, so that the line profile is the square of the ordinary line shape. Thus the line width is reduced by a factor of about 0.6 over that obtained by other methods.

An elegant way to reduce the unmodulated part of the probe beam is the technique of polarization spectroscopy, introduced by Wieman and Hänsch (*17*) (Fig. 6). It is like saturation spectroscopy in that Doppler broadening is eliminated by using a saturating beam and a probe beam which pass through the sample in opposite directions. However, the probe beam is plane-polarized and encounters a polarization analyzer before reaching the detector. The saturating beam is also polarized, either linearly or circularly depending on the characteristics of the spectral line being studied, and so preferentially excites lower-state molecules oriented in some particular direction. The molecules that remain behind in the lower state are thus also oriented in the complementary direction to those that have been removed by excitation. Consequently, the medium becomes able to change the polarization of the probe beam, either changing its polarization from linear to slightly elliptical or rotating the plane of polarization. In either case, the effect of the saturating beam is to make it possible for the probe beam to pass through a polarizer which was set to

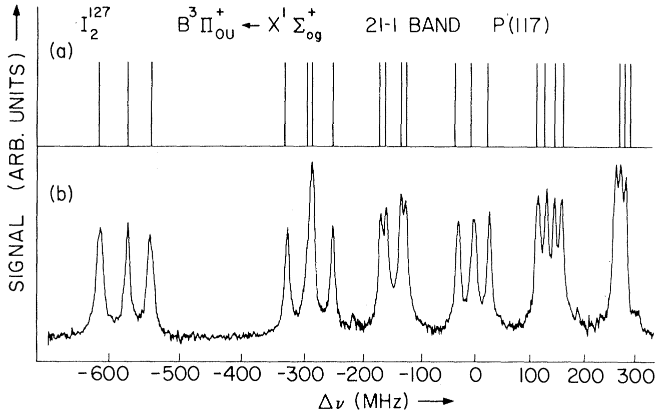
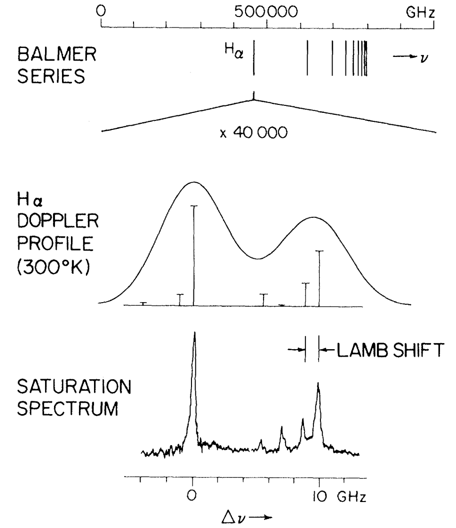


Fig. 3. Hyperfine structure of the *P*(117) 21-1 $B \leftarrow X$ transition of molecular iodine at 5682 nm; (a) theoretical; (b) experimental.



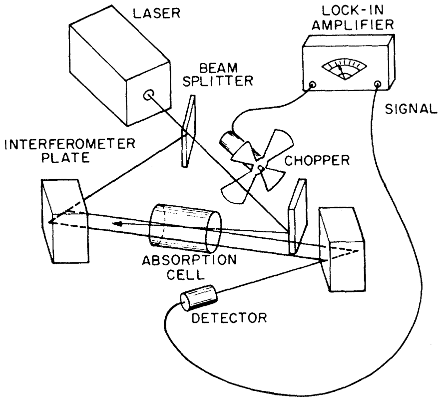
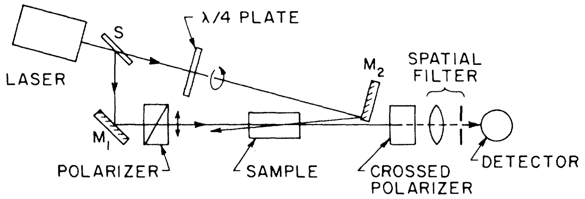


Fig. 4 (left). Hydrogen Balmer series and fine structure of the red line H$_\alpha$ resolved by saturation spectroscopy. Fig. 5 (right). Apparatus for spectroscopy by saturated interference.

Fig. 6. Apparatus for Doppler-free polarization spectroscopy.



block it. In that case, or even if the analyzer had been offset by a small amount to let through a small amount of the probe beam, there is a large intensity change with a greatly reduced background, and consequently the signal-to-noise ratio is improved dramatically. When the probe polarizer and analyzer are not quite crossed, the signal decreases on one side of the line center and increases on the other side. This dispersion shape can be helpful when it is desired to lock a laser to the center of the spectral line.

Hänsch and his associates have used the polarization technique in several investigations of the visible Balmer lines of hydrogen. The increased sensitivity of this method, compared to the earlier saturation technique, made it possible to reduce the pressure and current in the discharge cell where the excited hydrogen atoms are produced and studied. It also permits a reduction in the laser intensity, which helps in avoiding power broadening. Figure 7 shows the improvement in resolution of the hydrogen H_α line, obtained by saturation spectroscopy and polarization spectroscopy with a highly monochromatic continuous-wave dye laser (*18*). It can be seen that some components do not appear when the polarization method is used. These are transitions for which the lower level is so symmetrical (a state of zero total angular momentum) that it cannot be polarized. There are times when eliminating some components makes a useful simplification: in other cases, it is necessary to resort to saturation spectroscopy without polarization to reveal particular components.

It is interesting to consider polarization spectroscopy as a special case of saturated interference spectroscopy. Linearly polarized light is equivalent to a superposition of right and left circularly polarized beams of equal amplitude and phase. The saturating beam changes the amplitude or phase (or both) of one of these component beams and, therefore, changes the resultant by either rotating the plane of polarization or making the polarization elliptical. Before saturation, the components of the electrical field perpendicular to the resultant plane always canceled, but after saturation that cancelation is incomplete. It may well be that other kinds of two-beam interferometers might be used for saturated interference spectroscopy. However, the polarization technique is probably simpler and less subject to mechanical vibrations than most other ways in which two component beams can be combined.

Two-Photon Spectroscopy Without Doppler Broadening

In 1970 Vasilenko, Chebotayev, and Shishaev (*19*) proposed a method of observing two-photon transitions free from Doppler broadening. As is well known, electromagnetic waves cannot easily change a molecule from an initial state to another state of the same parity. If, however, the molecule is subjected to two light waves whose quantum energies add up to the amount needed for the change, they may combine to produce a two-photon transition. You can think of one of the beams as polarizing the molecule at its light frequency, to a large enough extent that the molecule becomes capable of absorbing the other beam to complete the transition to the upper state. In the method of Vasilenko *et al.*, the transition takes place by the absorption of one photon from each of two beams which travel through the medium in opposite directions. For a molecule that is moving with velocity component v along the direction of one of the beams, the frequency of that beam is shifted downward to $(1 - v/c)\nu$, while the other beam is shifted upward to $(1 + v/c)\nu$. The sum of frequencies of the two waves, and hence the sum of their quantum energies, is unchanged by the motion of the molecule. In other words, the equal and opposite Doppler shifts of the two waves cancel out when the sum of the frequencies is taken. That is enough to ensure that if the sum of the wave frequencies is resonant for one molecule, it is resonant for all of them regardless of their motions.

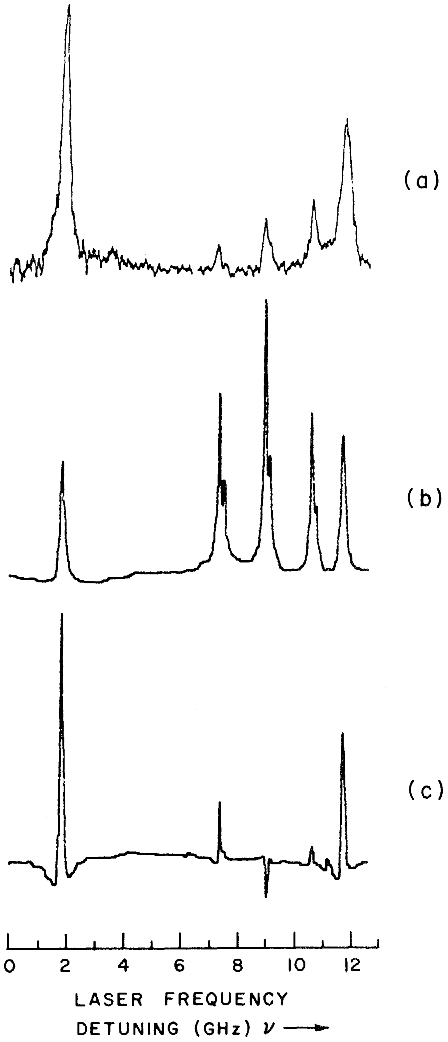


Fig. 7. Fine structure of the hydrogen H_α line obtained by (a) saturated absorption with a pulsed dye laser, (b) saturated absorption with a continuous-wave dye laser, and (c) polarization spectroscopy with a continuous-wave dye laser. [Courtesy of J. E. M. Goldsmith, E. W. Weber, and T. W. Hänsch]

Two-photon Doppler-free spectra were observed by this remarkably simple method nearly simultaneously by Biraben, Cagnac, and Grynberg (*20*), Levenson and Bloembergen (*21*), and Hänsch, Harvey, Meisel, and Schawlow (*22*). Each of these groups observed two-photon transitions in atomic sodium, from the ground 3*s* state to 5*s*, or 3*s* to 4*d* states. The arrangement used by Hänsch, Harvey, Meisel, and Schawlow (*22*) is shown in Fig. 8. The laser beam is reflected by a mirror to produce the second beam traveling in the opposite direction through the gas. The two-quantum absorption is detected by subsequent ultraviolet fluorescence, which could not be produced by the absorption of a single quantum of visible light.

Lee, Wallenstein, and Hänsch (*23*) observed Doppler-free two-photon transitions between the 1*s* and 2*s* states of atomic hydrogen, using the second harmonic of a pulsed, visible dye laser. The fundamental of the dye laser, near 486 nm, was used to probe the Balmer β ($n = 2$ to $n = 4$) line by saturation spectroscopy at the same time. Thus it was possible to measure the difference between the 1*s* to 2*s* transition frequency and four times the 2*s* to 4*p* frequency. On the Dirac theory of the hydrogen atom these should be equal, but they differ slightly because of the Lamb shift of the two atomic states, especially the lower one. This experiment, and a subsequent improved version by Hänsch and Wieman (*24*), gave values of the Lamb shift of the ground state in good agreement with calculated values from quantum electrodynamics. The present experimental error, about 29 MHz in a Lamb shift of 8159 MHz, is mainly caused by limitations of the laser, which can be greatly reduced. Ultimately, it should be possible to take advantage of the extreme sharpness of the 1*s* to 2*s* transition which connects two long-lived states and should therefore have a width of about 1

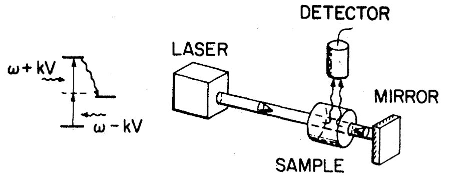


Fig. 8. Apparatus for Doppler-free two-photon spectroscopy.

Hz, or less than one part in 10^{15}. It should, thus, be possible eventually to measure the wavelength of this line to about 1 percent of its width, or one part in 10^{17}. But nobody can measure anything to one part in 10^{17}. Obviously much work remains to improve techniques and standards to extract all the information from such a very narrow line. Long before that, a precision measurement of the isotope shift will yield an improved measurement of the ratio of the mass of the proton to that of the electron.

However, factors other than laser line width and first-order Doppler broadening stand in the way of obtaining the ultimate very high resolution. There is a second-order Doppler broadening, of magnitude $(v/c)^2$ or about one part in 10^{11}, even for atoms moving transversely to the direction of observation. The atoms move quickly through the laser beam, and therefore the spectral lines acquire a width inversely proportional to the interaction time. Lasers can be used in ways that help to overcome the transit time broadening. For instance, the atoms may be required to interact with several laser beams one after the other. Then it is the longer transit time through the whole system, and not just through an individual beam, which determines the ultimate line width (*25*). Alternatively, the laser may be repetitively pulsed, as by mode locking (*26*).

Second-order Doppler broadening can be reduced only by decreasing the speed of the atoms under study. For some substances such as hydrogen, this can be done by cooling them to cryogenic temperatures, but many other materials condense if they are cooled appreciably below room temperature. But cooling to very low temperatures can be done by radiation from another laser (*27*). In this proposed method, atoms lose momentum and slow down by scattering photons from a light beam coming in the opposite direction. The cooling laser would be tuned a little below the resonant frequency for which light is scattered most strongly by the atom. Then if the atom is moving in a direction opposite to the light beam, it sees the light frequency as shifted upward into resonance with it, and so scatters the light strongly and is slowed down. An atom moving in the opposite direction would find the laser frequency shifted downward, out of resonance, and so would not be affected by the light. Thus, even if the light comes in over a wide range of angles, it only scatters strongly from those atoms that are slowed down by the scattering, as long as the light frequency is below the resonance frequency for stationary atoms. In that way, the radiation pressure of the light acts to slow down atoms and reduce their temperature.

Simplifying Spectra by Laser Labeling

Optical spectra of complex atoms and molecules are greatly complicated by lines from different energy levels being close together. This comes about because the frequency or wavelength of a spectral line is determined only by the difference in energies of the upper and lower levels, not by their absolute values. Absorption of laser light, however, can alter the population of a chosen atomic or molecular level and so make it possible to recognize all of the lines from just that particular level. For instance, if a monochromatic laser excites atoms to an upper, previously empty state, the subsequent fluorescence will come from just the chosen upper state to various lower levels. Moreover, during the short time between excitation and fluorescence, a new set of absorption lines can be observed, which are transitions starting on the newly populated level and going to still higher levels. The absorption from the upper levels can be recognized because it lasts only a short time, ranging from nanoseconds to milliseconds, after pulsed excitation, and so will not be seen if the probe pulsed beam is appropriately delayed. Alternatively, the two-stage excitation can lead to a distinctive fluorescence at a shorter wavelength or to ionization that can be detected electrically. For example, Paisner, Solarz, Worden, and Conway (*28*) have used three-step excitation with three pulsed dye lasers, to analyze the high-lying states of rare earth and actinide atoms.

It is also possible to label a low-lying level, by decreasing the number of molecules in that level through optically pumping them to some higher level (*29*). When light from an intense pump laser is absorbed by the medium, it excites molecules from some particular lower state and thereby reduces the population of that state. Consequently, the absorption coefficient will be reduced for all absorption lines originating from the chosen lower level. If the pump laser is turned off and on by a mechanical chopper, a probe beam from a tunable laser will be modulated whenever it is tuned to any absorption line from the level whose population is being modulated. Other lines in the same region will not be modulated and hence will not show up on a phase-sensitive detector locked to the chopping frequency. Thus Kaminsky, Hawkins, Kowalski, and Schawlow (*29*) were able to pick out a sequence of vibrational lines in the Na_2 A ← X band spectrum, even though some of them were seriously displaced by perturbations.

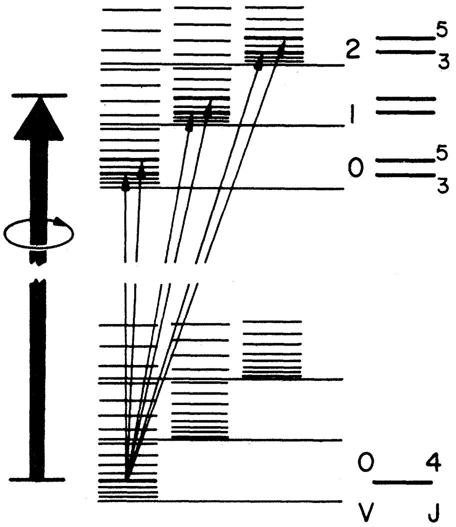


Fig. 9. Energy levels and transitions for polarization labeling.

This method of labeling a lower level by modulating its population is quite similar to the saturation spectroscopic technique of Fig. 2, except that the probe beam comes from a second laser which is tuned to wavelengths other than the pumping laser line. Similarly, the polarization method of Fig. 6 can be adapted for labeling (*30*). The pump beam alters the average orientation of the molecules in the selected lower state, so that the medium becomes doubly refracting at the wavelengths of all of the absorption lines starting from that level, as is indicated in Fig. 9. Then if the probe beam's polarizer and analyzer are crossed, light can reach the detector only at these wavelengths. It is then possible to photograph the labeled spectrum, with the aid of a probe laser that either emits a broad band of wavelengths or is scanned in wavelength during the exposure. No light comes through the crossed polarizers except at the wavelengths where the medium has been made doubly refractive by orienting molecules with the particular lower level. The labeled absorption lines then appear as bright lines on a dark background, as shown in Fig. 10. For a diatomic molecule, such as sodium oriented by a circularly polarized pump beam, a series of doublets is observed. For each upper-state vibrational level, two transitions are seen, for which the rotational quantum number of the initial state is either decreased by one unit (P branch) or increased by one unit (R branch). As the pump laser is tuned, different levels are labeled and different sets of doublets are seen, each corresponding to a different value of the lower-state rotational quantum number, J. Within each series, the intensities of the doublets vary because of the Franck-Condon factors, but each group stops abruptly when the upper-state vibrational quantum number, v', is zero since that is the lowest possible value of v'. Thus polarization labeling can quickly provide enough information to assign quantum numbers and derive constants for a unknown electronic state of a molecule.

Saturation labeling and polarization labeling are likely to be most useful for resolving the greater complexity of polyatomic molecules. Teets (*31*) has applied polarization labeling to assign rotational quantum numbers of some levels in NO_2. Still more complicated molecules could be simplified by labeling techniques, most especially by using an infrared laser for pumping. In sufficiently complex molecules, the spectrum can be so dense that the spacing between lines is less than the natural line width determined by the lifetimes of the excited states. Then one could not avoid pumping more than one level, no matter where the pump laser is tuned. The labeled spectrum would then contain the lines from the two or more pumped levels. To separate them, a second laser could be used to pump one of the absorption lines labeled by the first laser. Any line that is labeled by both pump wavelengths must then originate on their common lower state. The two lasers could be used simultaneously with different chopping frequencies, so that the other lines would be modulated at the sum of the chopping frequencies and thus easily recognizable.

Coherent-State Techniques

So far, we have been considering ways to find, resolve, and identify the stationary states of atoms and molecules. However, a short pulse from a laser can put an atom or molecule into a coherent superposition of several levels. In such a superposition, the atom or molecule can have a motion, either rotation or vibration, at a frequency corresponding to the difference in energy of the levels (divided by Planck's constant to put it in frequency units). For instance Haroche, Paisner, and Schawlow (*32*) used a laser pulse wide enough to excite a superposition of several hyperfine levels in the $6p$ state of atomic cesium. The combined state has a magnetic moment, which causes it to precess in the field of the nucleus. Thus the fluorescent light's polarization oscillates at the hyperfine frequency. If it is observed through a polarizer, the intensity of the decaying light pulse is modulated at the hyperfine frequencies of the $6p$ state. From these oscillations, the hyperfine splittings can be determined.

Many beautiful experiments have been carried out on laser-induced coherent states. These include such phenomena as photon echoes (*33*) and free induction decay (*34*). A particularly attractive way to get the short pulse interaction times, which are needed to set up coherent states if relaxation is fast, is to use frequency switching (*35*). The laser is tuned just off the line to be excited, and then either the laser frequency is suddenly shifted into resonance or a change in an applied electric field tunes the atom or molecule into resonance with the laser.

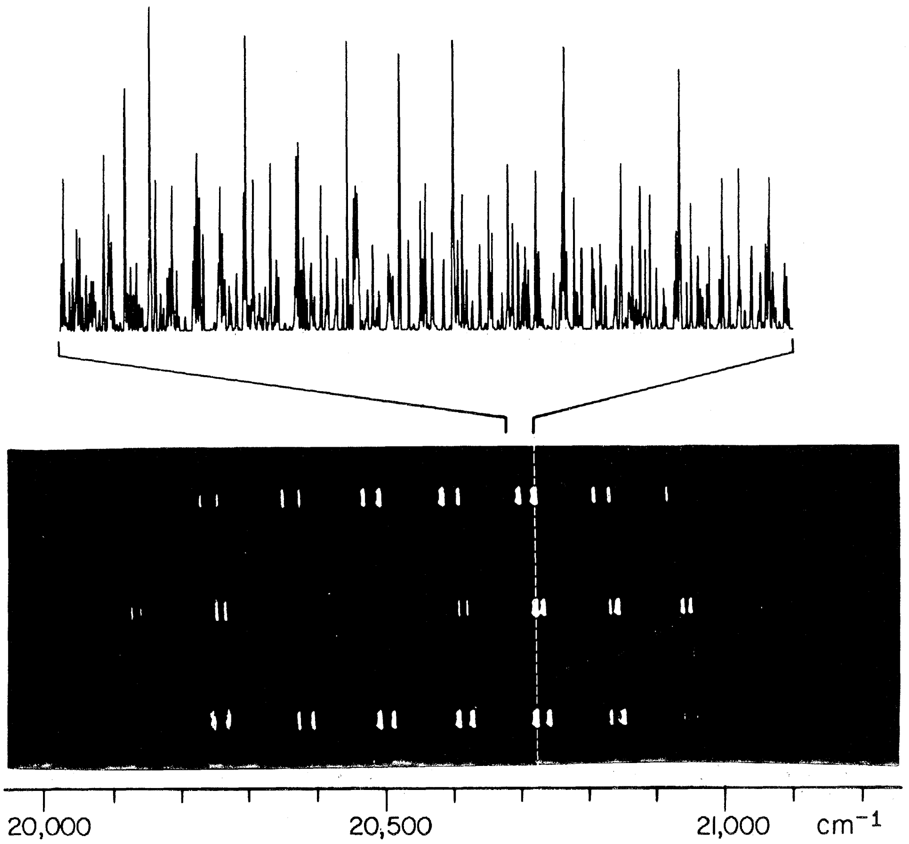


Fig. 10. Polarization-labeled spectra of Na_2 B $^1\Pi_u$ band.

Conclusions

There are really far more new laser techniques, and spectroscopic experiments with them, than can be covered in an article of this length. Nevertheless, these examples show that lasers can now be used to probe optical spectra and resolve structures to the limits set by the natural widths of the spectral lines. The sensitivity is great enough so that observations can be made at pressures low enough for pressure broadening to be negligible. Doppler widths can be eliminated by using the intensity of the laser beam in a number of different ways. Similarly, the intensity of the laser light makes possible labeling techniques that pick out the absorption or emission lines from a chosen level, and thus simplify complicated spectra.

For some regions, especially in and near the visible portion of the spectrum, continuous wavelength coverage is now available. Even there, it is not always easy to get the desired laser properties such as intensity of the wavelength needed. It is still often necessary to fit the problem to the available laser and to look for a molecular absorption at the convenient wavelength to try out a new technique. Especially for shorter ultraviolet wavelengths, we still lack good, powerful, monochromatic lasers for high-resolution spectroscopy. However, progress is still rapid and more techniques are becoming conveniently available for use on problems of physical, chemical, or even biological interest.

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Stabilized Lasers and Precision Measurements

J. L. Hall

With the pervasive spread of lasers in scientific research, industry, and education, it may be interesting to consider a laser field that has been active since the very beginning of the laser era but that is just now coming toward fruition. This research area is concerned with precision measurements made with the use of stable laser techniques. Indeed, the laser pioneers Charles Townes, Ali Javan, Art Schawlow, and Bill Bennett were well aware of the possibilities of making precision measurements with their lasers. I can remember the audience excitement at the 1962 American Physical Society meeting when Javan played a tape recording of the actual audio beat frequency between two of those early optical masers (*1*). The spectral width of those masers was below 100 hertz, and their optical frequency was about 3×10^{14} Hz. It was clear to everyone that it would be possible to do experiments of unprecedented resolution with these new sources. Indeed, after more than 15 years of work by a large number of dedicated people, this situation is now approaching reality.

In this article I trace the concepts that have led to the present circumstance where in perhaps six laboratories in the world a useful resolving power of about 10^{-11} is possible and in perhaps another dozen laboratories it is possible to make measurements of time-averaged quantities in this domain and below. Although this capability now is mainly confined to national measurement laboratories, the development and availability of commercial equipment based on some of these concepts is bringing a new interest and capability into the hands of the larger scientific community. Thus we may look forward in the next few years to an explosive growth in the application of laser frequency control techniques to precision measurements.

Introduction of Frequency Metrology into the Optical Domain

In view of the demonstration by Javan and his colleagues (*1*) of a laser fractional spectral width of about 10^{-13} and an earlier experiment by Cedarholm and Townes (*2*) which showed that the frequency of an ammonia maser was independent of the direction of motion of the ammonia molecules to a precision of better than 10^{-12}, it seems quite natural that these researchers at the Massachusetts Institute of Technology (MIT) would turn to a laser version (*3*) of the Michelson-Morley experiment.

In the 1887 "ether drift" experiment of Michelson and Morley (*4*), a path length of 36 feet (11 meters) was multiply folded onto a 5-foot sandstone optical table floating in mercury. The earth's orbital velocity gives a value for $(v/c)^2$ of $\simeq 10^{-8}$ (where v is the earth's orbital velocity and c is the speed of light), and so an expected path length change for the "ether shift" of about 0.4 fringe for Michelson's apparatus. His readings did not exceed 0.02 fringe. In spite of the consequences of this null result (the invention of the special theory of relativity by Einstein, Lorentz, and others) and the significance of potential improvements in this experiment, no major advances were made for 77 years. Basically the experiment was limited by the techniques of length measurement: one cannot subdivide interferometric fringes forever with the use of ordinary techniques. The MIT group took advantage of the optical heterodyne process—made prac-

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The author is on the staff of the Joint Institute for Laboratory Astrophysics, National Bureau of Standards and University of Colorado, Boulder 80309.

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