

SPECTROSCOPY WITH TUNABLE LASERS IN THE VISIBLE REGION

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ABSTRACT

The several kinds of tunable lasers and some methods for making them really monochromatic are reviewed. Gas lasers, and particularly ion lasers tunable over several thousand MHz, have been used by Hänsch, Levenson, and Sorem for saturation spectroscopy on a number of lines of molecular iodine. The absorption cell is external to the laser. It is found that the quadrupole coupling parameter is nearly independent of the molecular rotation and vibration state, but the magnetic hyperfine structure constant is large for states near the dissociation energy. For broader tunability dye lasers have been investigated. Holzrichter and Macfarlane used a tuned flashlamp-pumped dye laser to generate excitons and magnons in anti-ferromagnetic MnF_2 . The growth and relaxation of these excitations is observed through the magnetization produced in the crystal. Several experiments have been done with dye lasers pumped by a pulsed nitrogen laser. These include amplification of an entire image with good resolution, preserving wavelength, obtained by Hänsch and Varsanyi. Laser action has been obtained for several dyes in gelatin. Ways have been found by Hänsch to make a pulsed tunable dye laser extremely monochromatic, and coherent beams no wider than 7 MHz have been generated. Hänsch and Shahin have

applied this laser, with the external cell method of saturation spectroscopy, to resolve hyperfine structures in the atomic sodium D lines. By delaying the probe pulse after saturation, the restoration of equilibrium has been studied both with and without a buffer gas. In the latter case, a narrow transmission band remains for at least several hundred nanoseconds after the saturating pulse.

Lasers are still very primitive devices. The only thing that saves us most of the time is that, being physicists, we are not assigned a task to do with the lasers but are rather able to do whatever can be done with the available lasers. We have been quite resourceful in adapting to the limitations of the laser and doing what is possible with the existing ones. But we are however now entering a time, I think, when some of these limitations are being overcome, and in particular, the limitation on tunability. (I should restrict my discussion to the visible and near-visible region. Others at this symposium have discussed the problems in the infrared.) As an example of some of the difficulties, a few years ago we wanted to do some work on photochemistry and the only way we could do it was to find a molecule which had lines coinciding with an available laser. At that time there was the ruby laser, which we could tune over about 9 cm^{-1} by changing the temperature. To match that ruby laser we had to use bromine which turned out, after some years, to be a most unfortunate choice from the point of view of photochemistry but that was all we could do with the available lasers [1, 2]. Similar restrictions are encountered with other lasers which have a rather narrow tuning range, and the only way that we could use them for spectroscopy was to find something which happened to coincide with their particular laser lines.

Let us first discuss an experiment that we have done recently in that way. We used available argon and krypton ion lasers and found a molecule which happened to coincide with their output wavelengths, in particular, the iodine molecule. The method used in these experiments, which were done by Hänsch, Levenson, and Sorem [3, 4] is a method of saturation spectroscopy. The technique used was developed out of earlier work by Hänsch and Toschek [5] and was recently introduced in different context by Borde and by Smith and Hänsch [6]. A scheme of the experiment is shown in Fig. 1. The advantage of an argon or krypton ion laser is twofold. It has quite a lot of power so that we can get saturation outside the laser. Also the spontaneous emission lines are rather broad, so that we can tune over perhaps 5000 MHz. The light from the laser is split into two parts at the beam splitter. One part, which we may call the saturating beam, is chopped. It goes through the iodine cell and bleaches its way through. The other part, which we call the probe beam, goes through in almost exactly the opposite direction. In

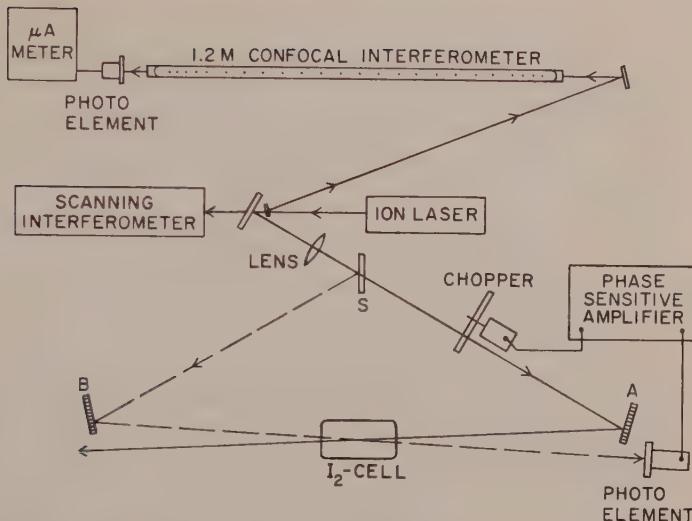


Figure 1. Saturation spectrometer for iodine hyperfine structures.

Fig. 1, the angle between the beams is exaggerated, as it is of the order of 1 mrad. If these beams affect the same molecules, then the saturating beam will bleach a path for the probe beam and the signal at the photodetector will increase. Thus, as the saturating beam is chopped, the light reaching the photodetector is modulated. Now this happens, of course, only if the two beams are seeing the same molecules. That happens most simply if the laser is tuned exactly to the center of the resonance line so that its output is absorbed by molecules which are going neither to the left nor to the right, but only transversely to the beam. For those molecules, neither beam is Doppler shifted and the two beams are in resonance with the same molecules. So, in that way, as is familiar in saturation spectroscopy, we get rid of the Doppler broadening. One of the advantages of this method is that it is convenient to work outside the laser, and particularly so if you want to work in a magnetic field. Although it will not be discussed here, we have recently begun work on the Zeeman effect of these saturation resonances in iodine.

The laser is made to oscillate in a single axial mode by a quartz etalon, thermostatically stabilized. The frequency is scanned by a piezoelectric drive on one end mirror. As the scan rate may not be constant, it is calibrated by passing some light from the laser through a 1.2-m confocal interferometer.

In this experiment, we are looking at single rotational lines in the vibrational bands of the transition from the ground $^1\Sigma_{0g}$ to an electronically

excited state $^3\Pi_{0u}$. There are an enormous number of lines in these bands, but we can study only those few absorption lines which happen to coincide with one of the wavelengths produced by one of our lasers. Fig. 2 indicates the kind of hyperfine structure we may expect to find. The hyperfine splittings are primarily due to the quadrupole moment of the I_2^{127} nuclei and secondarily to a magnetic hyperfine interaction. There are two nuclei which have spin $5/2$ for the ordinary isotopes of iodine. The hyperfine interaction Hamiltonian is

$$\mathcal{H}_{\text{hfs}} = \sum_{i=1}^2 eQq \frac{\frac{3}{2}(\vec{I}_i \cdot \vec{J})^2 + \frac{3}{2}\vec{I}_i \cdot \vec{J} - |\vec{I}_i|^2 |\vec{J}|^2}{2J(2J-1) I_i(2I_i-1)} + C \vec{I}_i \cdot \vec{J}$$

Each nucleus couples independently to the field gradient and the energy levels of the two nuclei simply add because there is very little coupling between the nuclei directly. For one nucleus you will have states with $m_I = \pm 1/2, \pm 3/2$, and $\pm 5/2$. In an axially symmetric field gradient the level spacings are in the ratio 1 to 2 so that the energies are 0, 1, and 3. If you have two such nuclei, you just simply add up the energies in all possible combinations and the third column of Fig. 2 shows what you get. There are five equally spaced levels and then a double spacing. This is what you would get if there were no magnetic couplings, no magnetic $\vec{I} \cdot \vec{J}$

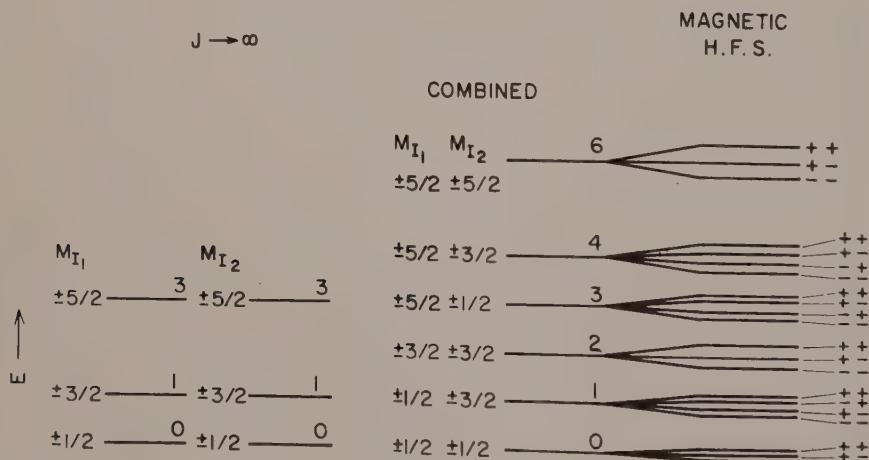


Figure 2. Expected hyperfine level pattern from quadrupole and magnetic interactions (for states with large J).

term, and also if the rotational angular momentum J were infinite. Actually in some of these lines observed it is pretty close to it. We have observed lines with J values as high as 117. That is very large. If the $\vec{I} \cdot \vec{J}$ term is small but appreciable, these levels split further, as shown in the last column, producing triplets and quartets. The selection rules are extremely simple in that the nuclear orientations do not change in the transition, so that the pattern of the lines is just the same as the pattern of the levels. In other words, we have an upper state with the sort of pattern shown in Fig. 2 and a lower state with the same kind of pattern. Each level in the upper state connects with the corresponding level of the lower, so that the line pattern is just the same as the level pattern. No crossover transitions are observed. Thus only the difference of the quadrupole couplings for the two electronic states can be observed in most lines. Hyperfine structures of iodine lines coincident with the 6328-Å helium-neon laser line have been observed and analyzed by Hanes and Dahlstrom [7, 8].

Fig. 3 shows the observed hyperfine structures of two molecular iodine

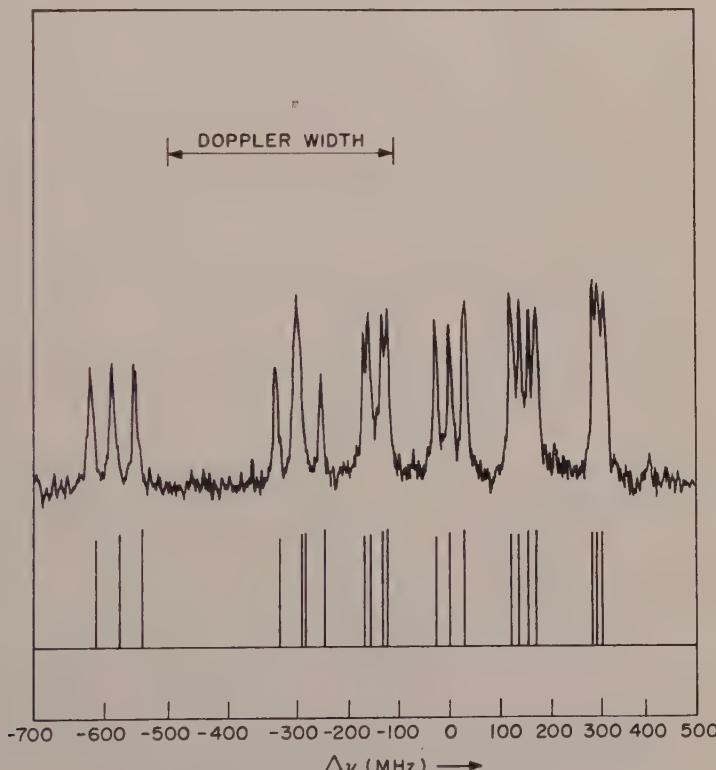


Figure 3 (a). Hyperfine structure of $I_2^{127} P(117)$ 21-1 line.

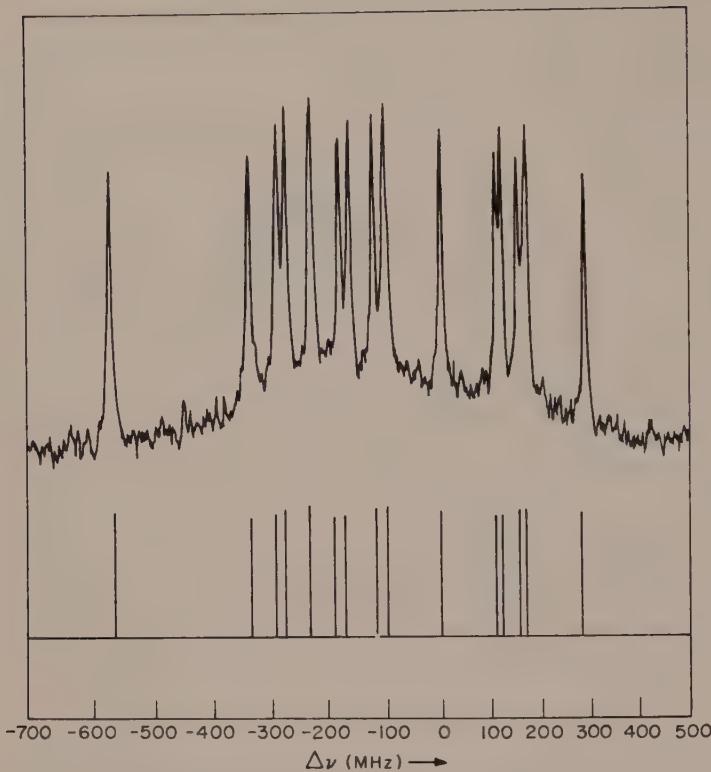


Figure 3 (b). Hyperfine structure of I_2^{127} R(78) 40-0 line.

lines, where the J values of the lower state are respectively odd [Fig. 3(a)] and even [Fig. 3(b)]. In the latter case, the Pauli exclusion principle prevents states where both nuclei have the same quantum numbers. Then all triplets become singlets and so the number of components in the hyperfine pattern is reduced from 21 to 15.

It is worth noting that some individual components are strong, well-resolved, and have a width of about one part in 10^8 . It should be fairly easy to lock the laser onto one of the components with a precision of about 1% of the linewidth, so that we would have a convenient laser standard in the green or in the yellow reproducible within a part in 10^{10} . This modulation method is quite sensitive and gives a good signal-to-noise ratio.

By using the argon and krypton lasers and all the available lines, and also using the radioactive iodine as well as the normal one, we can get

measurements of the quadrupole coupling for a number of lines. It is found that the difference in eQq varies by only about 100 out of 2400 MHz over the range of lines observed. The $\vec{I} \cdot \vec{J}$ coupling, though, does vary quite considerably. In Fig. 4, the magnetic hyperfine interaction constant is plotted against the energy of the upper state above the bottom of the $^3\Pi_0$ band. It is expressed as $G = CI/\mu$, in order to correlate data obtained with two different

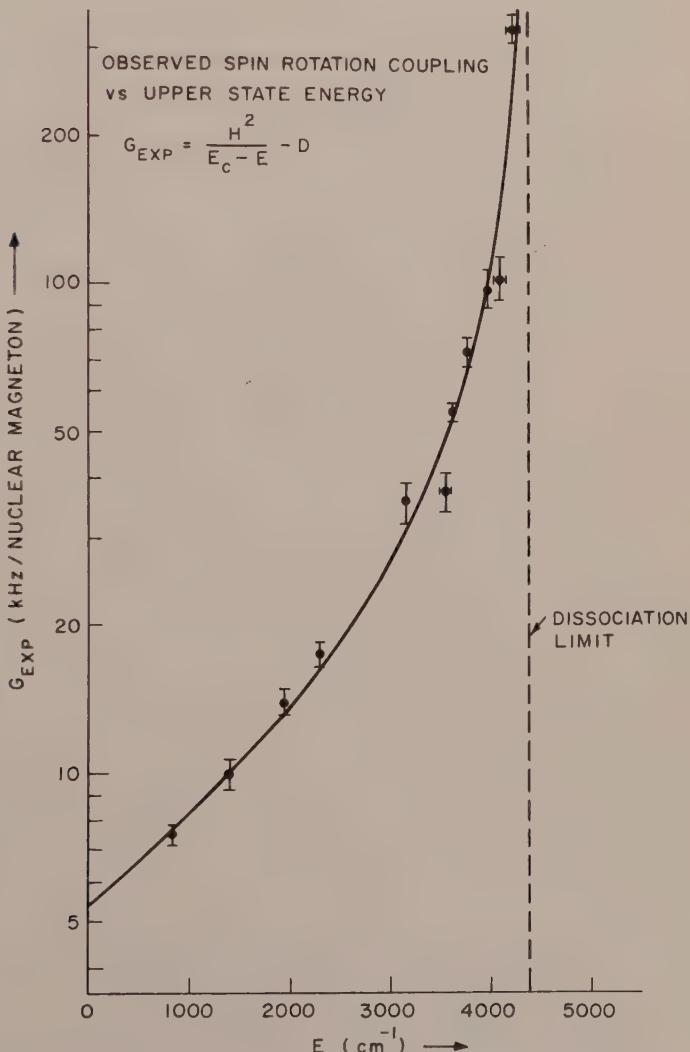


Figure 4. Magnetic hyperfine interaction as a function of the energy of the upper state above the bottom of the $^3\Pi_0$ band.

isotopes which have different spin and nuclear moments. Near the dissociation limit, the $\vec{I} \cdot \vec{J}$ coupling becomes very large, most likely because it comes about largely from mixing in another state which is close to that limit.

At low J values you can do something about separating the quadrupole couplings in the upper and lower state. The experiments show that the quadrupole coupling does not change much with either rotational or vibrational states. Thus, it is reasonable to assume that q_M , the field gradient along the molecular axis, is constant within a given electronic state. The measured quadrupole coupling is $e q_J Q$, where q_J is the corresponding quantity averaged over the rotation and so oriented along J . They are related by $q_J = q_M/[2 + (3/J)]$. It follows that by measuring the difference in quadrupole coupling for two known lines, we can solve for q_M in the upper and lower electronic states. Although the errors are large, we find $eQq = -2700 \pm 400$ MHz for the ground electronic state of I_2^{127} and $eQq = -800 \pm 400$ MHz for the $^3\Pi_0$ electronic state.

It is, however, somewhat frustrating that, in these experiments, we are able to study only those iodine lines that happen to lie near an argon or krypton laser line, and we would like, in particular, to look at some very low J values. The lowest J value that we have found so far is 10. We looked therefore at more broadly tunable lasers. So far, none of them is quite monochromatic enough to do justice to the fine structures in the iodine spectrum. However, parametric oscillators and dye lasers both provide tunable sources of coherent visible light. For both of them, progress is rapid, but at any frequency, extreme monochromaticity is not easily achieved when the device can oscillate over a wide range. Most of the visible can now be covered with tunable parametric oscillators and certainly a large part of the infrared [9]. One such device, based on the designs of Harris and available commercially, starts with a YAG:Nd laser which can oscillate at several wavelengths near 1μ , followed by a lithium iodate doubler, and a lithium niobate parametric converter. These lasers give pulses usually about $1 \mu\text{sec}$ in length with repetition rates up to a thousand per second. That is a fairly low duty cycle but for many experiments the high repetition rate makes it seem essentially continuous. The tuning range is a few hundred angstroms for each laser line. In all there is continuous tuning range of several thousand angstroms in the long-wavelength part of the visible region. With other versions, you can go further into the infrared.

We have, however, in our own work used instead what are to us rather simpler devices, the various kinds of dye lasers. The methods used for refining the monochromaticity and stability are largely applicable to other sources of coherent light.

A dye laser that was constructed by Holzrichter [10, 11] in our laboratory consisted of a cylindrical cell containing an organic liquid dye, with external mirrors. It was pumped by straight flashlamps which had

enlarged sections at the ends in order to provide a reservoir for pressure relief because these are flashed with a short intense current pulse. The circuitry was all coaxial to give a fast rise time. The laser produced pulses about 1 μ sec long and the peak power was a few kilowatts with sodium fluorescein dye. It was tuned by a diffraction grating which replaces one of the end mirrors. For finer tuning, the output mirror is replaced by a quartz etalon, and sometimes two etalons of thickness 0.5 mm and 2 mm. The laser output was thus reduced from a band of several hundred cm^{-1} to about 0.1 cm^{-1} with little loss of power.

This laser was used for an experiment in solid-state physics and in particular for studies of ions in crystals, for which the oscillator strengths are typically low. Thus a fairly large amount of pumping energy is needed to saturate any sort of an absorption. That is one reason for using a flashlamp-pumped laser. This particular one gave only a few millijoules but it is worth noting that Bradley has been able to get energy outputs of as much as 2 j in 1 μ sec out of flashlamp-pumped dye lasers, which is a power of several megawatts [12].

In the experiment of Holzrichter and Macfarlane, the laser is tuned to 5420 Å and used to excite excitons and magnons in manganese fluoride. Manganese fluoride is a crystal which is well known to be antiferromagnetic at low temperatures. That is, there are two sublattices with their spins arranged antiparallel. With the laser light you can raise some of the manganese ions, through a rather sharp absorption line at 5420 Å, to excited states and thereby change the spin. However, since this is a concentrated crystal the transitions are not strictly attributable to single ion transitions, but rather produce fairly narrow Frenkel excitons. The excitation is observed in this experiment through its magnetization detected by a pickup coil placed around the crystal. This is quite a difficult experiment and required a semiconductor preamplifier in the liquid helium to get a fast rise time, followed by additional amplifiers. Fig. 5 shows the apparatus.

By stressing this crystal, which has been extensively studied, the two exciton lines can be split so that the laser can be tuned to excite spins on either the one sublattice or the other sublattice. Moreover, the sharp exciton line is accompanied by spin-wave sidebands and if the laser is tuned a few angstroms, it can pump the spin-wave sideband. In that case, an exciton is produced on one sublattice and a magnon on the other sublattice. It was thus possible to measure relaxation times for both excitons and magnons.

This flashlamp-pumped laser can be refined and I believe that both the parametric oscillator and the flashlamp-pumped laser can be made as monochromatic as you need it to be, but you have to work for it. One problem is that the liquid in the dye cell becomes optically inhomogeneous under the intense heating of the flashlamp.

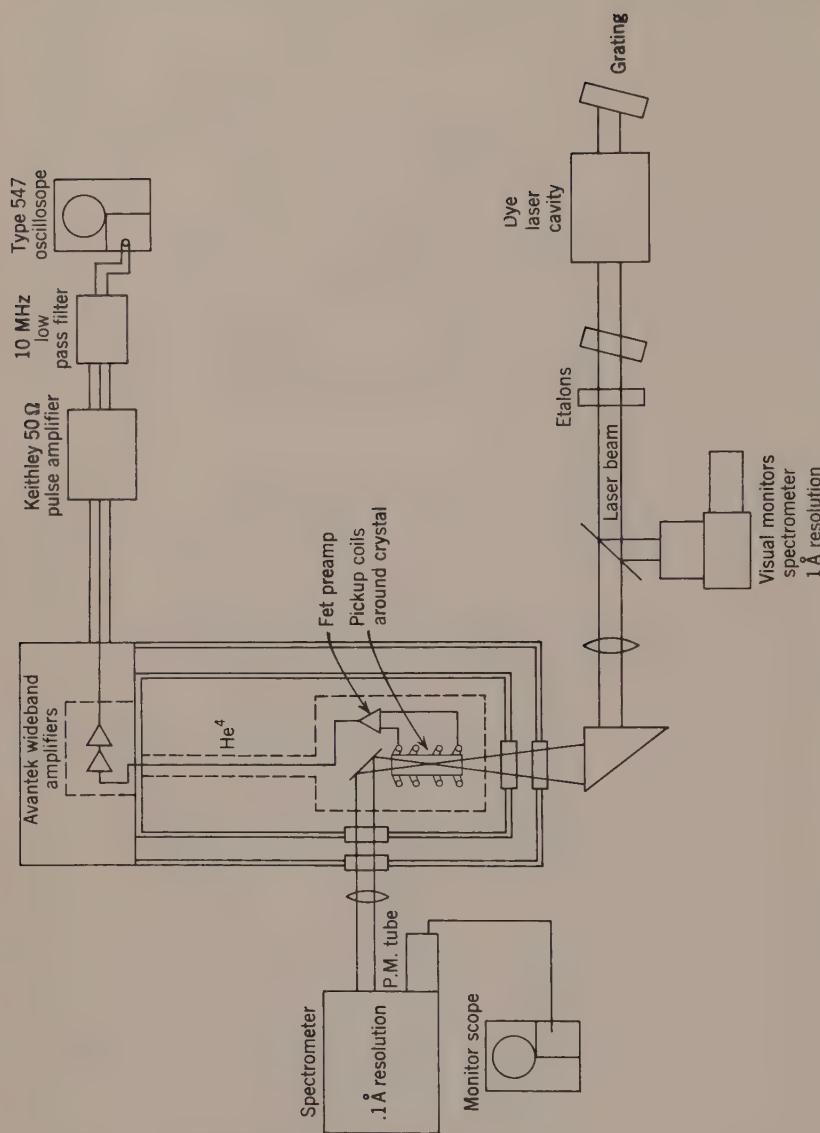


Figure 5. Apparatus for laser photomagnetism studies.

In many respects it is a lot easier to work, if you can, with a nitrogen laser. Nitrogen lasers are very effective for pumping dye lasers. They emit as a pump source in the ultraviolet at 3371 Å. The power output of one typical nitrogen laser is about 100 kW in a pulse which lasts about 10 nsec, or about as long as the excited states of typical dye molecules. It can be focused with a cylindrical lens to a line on the surface of the cell containing a dye, and many materials will lase under this kind of excitation [13]. I have been telling people for years that anything will lase if you hit it hard enough. If it has not lased yet, you have not hit it hard enough. This dye laser gives us a chance to prove our point. For example, following a suggestion of Mrs. F. Jurian, Tincture 99, Merthiolate (trade mark Eli Lilly and Company) was found to lase when pumped by the nitrogen laser.

To tune the laser you can put a diffraction grating at one end of the dye cell and a partially reflecting mirror at the output. As an alternative, an acousto-optic filter can be used for tuning the laser [14]. A wide variety of dyes have been discovered in the last few years and more are coming out all the time, so that laser action can be obtained at nearly any wavelength in the visible and near-visible region of the spectrum. There are some dyes which have tremendous tuning ranges. Methyl-umbelliferone, which forms an exciplex, fluoresces very strongly and will lase [15] from about 4000 Å in the violet, almost ultraviolet, right up into the green, beyond 5500 Å. So it is really a spectacular thing to turn this grating and see the color change so dramatically. Other dyes are used for other wavelength regions.

You can also take this dye laser output and pump other substances by end pumping. For example, when a blue beam from a nitrogen-pumped dye laser is directed into a single drop of fluorescein, a highly directional green beam emerges. This occurs since an extremely large gain is produced along the path traversed by the exciting beam, because of the large oscillator strength of the dye molecule transition.

With nitrogen lasers and with nitrogen-pumped liquid dye lasers as pumps, we have been able to obtain laser action from dyes in gelatin [16]. This provides further confirmation of our suspicion that nearly any substance will provide laser action if excited violently enough. It also provides the first edible laser material, if nontoxic dyes like fluorescein are used. Gelatin has long been used as an optical medium, particularly for color filters, and two commercial filters, Wratten 22 and 29, have been made to lase when pumped by a nitrogen laser. Moreover, gelatin is the base for most photographic films, so that complex film structures can be formed photographically. Thus Kogelnik and Shank [17] have shown that structures with periodic variation of refractive index, produced photographically in the gelatin medium, can provide selective reflection to tune laser action in the dyed gelatin.

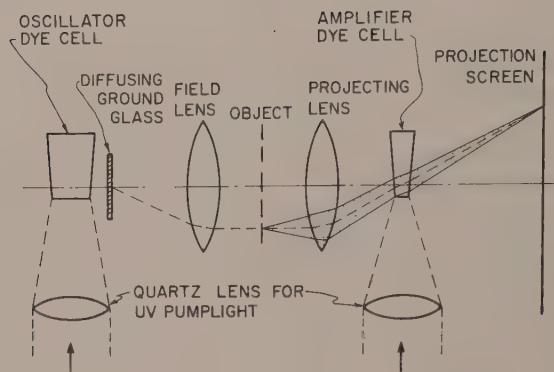


Figure 6. Arrangement for image amplification.

Hänsch and Varsanyi have shown that nitrogen-pumped dye lasers can provide high-gain high-resolution amplification of an entire image [18]. The device is not merely an image intensifier but a true amplifier by stimulated emission. Figures 6 and 7 show the arrangement. The source of light to be amplified is an oscillator cell which contains dye pumped by the nitrogen laser. It has to be rather bright, but not actually a laser. The light from the small spot source is collimated and passed through an object, which is a transparency, and then is focused by a projection lens onto the image screen. The amplifying cell is inserted between the projection lens and the screen, but at a place where the light has a small cross-section diameter. The dye is concentrated enough so that the pump light only gets in about a tenth of a millimeter so that the amplifying is done by a small volume of liquid on the edge of the cell, about a tenth of a millimeter in cross section. Even though the length of the dye cell is only 1.3 mm, the image is amplified by a factor of 100 to 1000 and the resolution is nearly diffraction limited for the 1/10-mm aperture. This high resolution is quite remarkable in view of the very high pumping intensity from one side of the cell. But refractive index changes from thermal expansion cannot occur before the short laser pulse ends, because the rate of expansion is limited by the velocity of sound. This kind of an amplifier is not a low light level device because any maser amplifier produces a lot of spontaneous emission, as has been discussed by many people. However, it could perhaps be made useful for large-screen displays. It has the remarkable property, in contrast to image intensifiers, that it does preserve wavelengths. The bandwidth of the rhodamine 6G dye that we used here is about 200 Å, but other dyes could

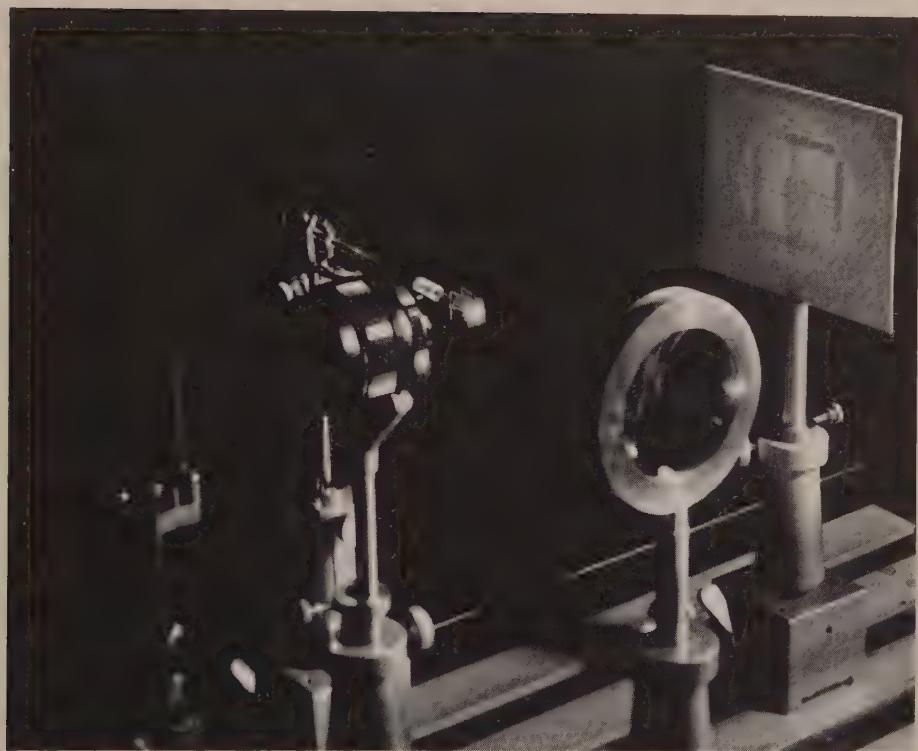


Figure 7. Photograph of image amplifier. The source is outside the picture to the left. The amplified image can be seen on the right.

give greater bandwidths with reduced gain.

The absence of thermal blurring in the image amplifier suggested that a well-collimated beam could be obtained from a dye laser cell. Such a beam would give sharply tuned reflection from a diffraction grating, whereas a range of wavelengths would be reflected for a beam broadened by refractive inhomogeneities. Hänsch [19] has shown that the effects of divergence from diffraction in the dye cell can be reduced and better collimation at the grating can be attained, by placing a telescope between the dye cell and the grating, as shown in Fig. 8. Moreover, the telescope illuminates a larger area on the grating, which also enhances the resolution. With this arrangement a linewidth of less than 0.1 \AA is obtained. A tilted quartz Fabry-Perot etalon, 6 mm thick with broadband reflecting coatings on each

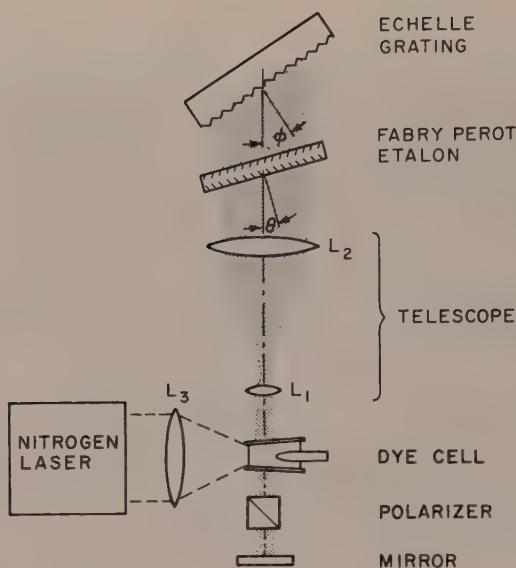


Figure 8. Monochrommatic tunable dye laser.

side, placed between the telescope and gratings, further narrows the output to about 300 MHz, or 0.01 cm^{-1} . This is less than the Doppler width of most spectral lines in gases. Fine tuning is obtained by tilting the etalon.

One of the things you have to remember in trying to make a pulsed dye laser really monochromatic is that the pulse is rather short. It is only about 10 nsec from the nitrogen laser and the dye really only gives good gain for about 5 nsec or so. Therefore, light only travels about 5 ft in that time and you simply cannot use a high-Q resonator structure that requires light to travel back and forth over a long distance because there just is not time enough for it during the pulse. And so rather than try and select modes here very well, Hänsch has used a structure which provides good wavelength selection essentially by putting in a highly filtering spectrograph into the laser. With rhodamine 6G, the gain is so high that the output mirror can have very low reflectivity, and the shortness of the pulse makes it nearly useless to increase the resonator Q for regenerative line narrowing. This dye laser is really a very simple device, but it will produce an output stable within $1/100 \text{ \AA}$ with pulses up to 100 times a second, and do this for hours on end.

However this is not yet narrow enough for high-resolution saturation spectroscopy. Therefore, to do saturation spectroscopy, Hänsch has added

to this a small passive confocal resonator with piezoelectric scanning. It filters to select a portion of the output. When you add the confocal resonator you do throw away some of the light, but the peak output power is about 1 W. To scan this device over a thousand megacycles or so, the grating is first set to the desired line, then the etalon is slowly tilted for the next finer tuning. The final fine tuning of the piezoelectric drive on the confocal resonator is synchronized by deriving its driving voltage from a potentiometer geared to the motor which turns the micrometer screw to tilt the etalon. This is a very simple method, but extremely effective, giving a linewidth of 7 MHz tunable over any desired range of about 2000 MHz. Incidentally, the confocal resonator lengthens the pulse from 5 nsec to 30 nsec by storing light in itself. With this device it has been possible, for the first time, to do high-resolution saturation spectroscopy experiments in an atomic vapor [20].

Figure 9 shows the apparatus used by Hänisch and Shahin for saturation spectroscopy of the D lines of sodium. As in the experiments of Hänisch, Levenson, and Sorem on iodine, a probe beam goes through the absorption cell one way and the saturating beam goes in the opposite direction. However, because the laser output fluctuates from pulse to pulse, an additional probe beam is used, which does not pass through the saturating region, and a differential amplifier corrects for fluctuations in the intensity of the laser beam. The sodium vapor used in this experiment is at a rather low pressure, about 10^{-7} Torr, but since sodium is a very strong absorber and has high oscillator strength, a power of a fraction of 1 W is sufficient.

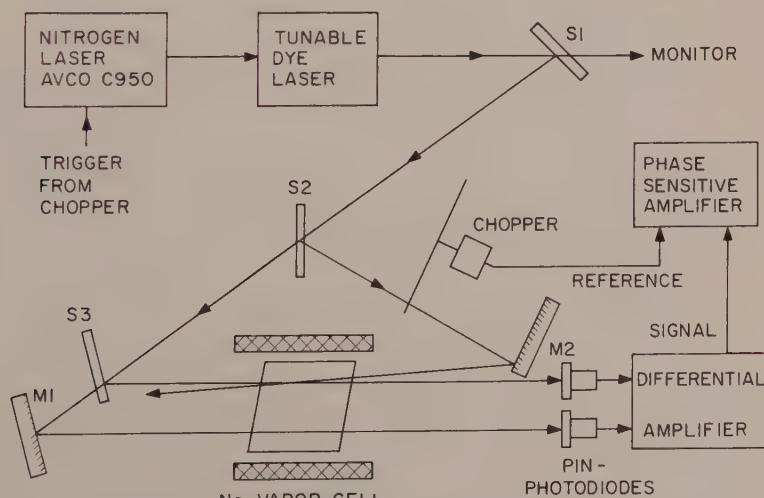


Figure 9. Saturation spectrometer for sodium.

Hyperfine structures in sodium have been studied extensively, and the ground-state $^2S_{1/2}$ splitting is 1772 MHz. The $^2P_{1/2}$ has a spacing of 192 MHz and that of the $^2P_{3/2}$ is enough smaller so that it is not resolved even in these experiments.

Fig. 10 shows the hyperfine structure of the D_2 line, $^2P_{3/2} \leftarrow ^2S_{1/2}$, observed by this method. On this scale, the other D line would be about 90 m away, and so it is evident that the dispersion and resolution are very high. It will be noted that there is an inverted bump, corresponding to enhanced rather than decreased absorption halfway between the two peaks. With this particular apparatus we are able to put to good use the fact that the laser is pulsed to investigate this phenomenon. The probe beam can be delayed by an optical delay line until after the saturating beam has gone. Figure 10(b) shows the saturated absorption when the probe pulse is delayed 700 nsec. The fluorescent lifetime is 20 nsec so that excited states have decayed long before the probe pulse arrives, and yet the bleaching remains, about half as much as it was originally. The reason for this is that after the

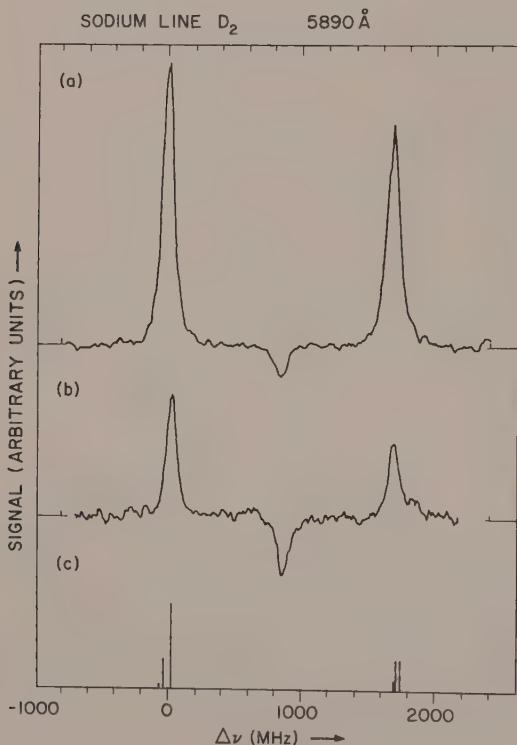


Figure 10. (a) Saturation spectrum of the sodium D_2 line without delay; (b) Like (a), but with a probe delay of 700 nsec; (c) D_2 hyperfine transitions.

saturating beam excites atoms from one hyperfine level of the $^2S_{1/2}$ state, the excited atoms fluoresce and make transitions partly to their original level but also in large part to the other hyperfine level of the ground state. Thus, the population in the first hyperfine level, for atoms with the particular velocity, remains reduced and consequently the absorption is reduced, until those atoms move out of the beam and are replaced by others.

This remanent spectral bleaching provides a very narrow filter which could have a fractional band width of perhaps 10^{-8} , or with better substances maybe even 10^{-10} . Moreover a saturation filter could be made to transmit an entire image. So it is possible to imagine this device, or something like it, as a kind of a velocity-gated viewer through which you could view a scene, illuminated by a laser searchlight which also bleaches the filter. Then you would be able to see light which comes back only from stationary objects. If the objects are moving you would not see them. Of course, you could offset the filter and see moving objects.

It can be seen in Fig. 10 that the enhanced absorption dip between the two peaks is stronger when the probe pulse is delayed. This dip is observed

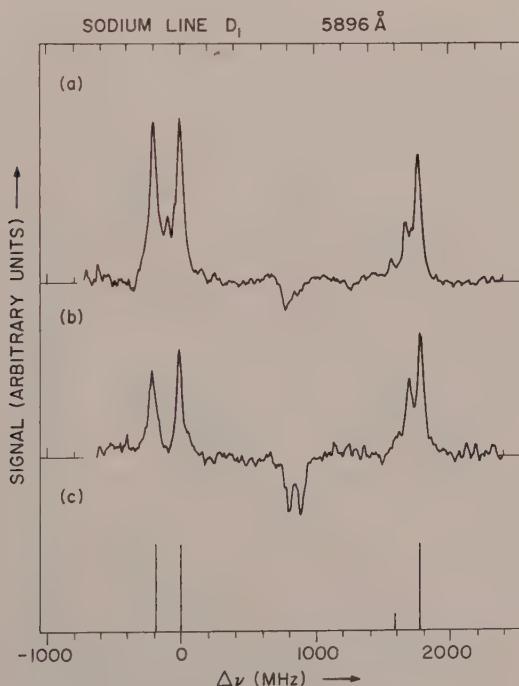


Figure 11. (a) Saturation spectrum of the sodium D₁ line without delay; (b) Like (a), but with a probe delay of 56 nsec; (c) D₂ hyperfine transitions.

when the laser, being tuned halfway between the transitions from the two ground-state levels, cannot interact with atoms having velocities perpendicular to the laser beams. However, there are some atoms which are moving with a component of velocity along the laser beam such that, to them, the saturating beam frequency appears to coincide with one of the transitions and the probe appears to coincide with the other. Then the probe beam will sense the enhanced absorption resulting from the optical pumping process just described.

Fig. 11 shows the line, $^2P_{1/2} - ^2S_{1/2}$, i.e., the sodium D₁ line. The splitting, 192 MHz, of the state is clearly resolved. Between each pair of upper-state components, there is a crossover transition, again caused by molecules which have the proper component of velocity along the beams. The relative intensities are as they should be from the selection rules. The saturation method rather exaggerates the differences, as the signal is proportional to the square of the oscillator strength.

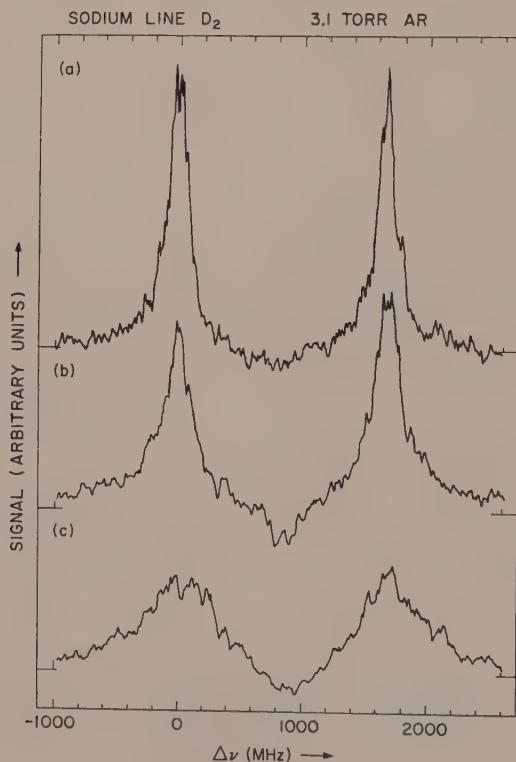


Figure 12. Pressure-broadened line shapes with 3.1 Torr of argon.
(a) Without delay, (b) 38-nsec delay, (c) 100-nsec delay.

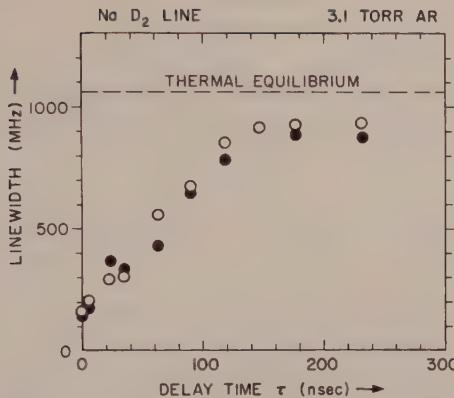


Figure 13. Linewidth of sodium hyperfine components as a function of probe delay time, with 3.1 Torr of argon.

With this apparatus it is now possible to study how the atoms restore their velocity distribution. The saturating pulse bleaches a few atoms which have nearly zero component of velocity in the direction of the beam. Thus these atoms are labeled so that their recovery can be studied. The kind of collisions needed to restore the absorption are those which redistribute the velocity distribution. Harder collisions, or more of them, are needed than, say, for microwave relaxation of polar molecules because the collisions have to restore the actual velocity distribution as the spin states are rather insensitive to collisions. Weak, rather distant, collisions are the commonest ones. It takes quite a lot of them to restore the equilibrium in velocity. One can tell something about the hardness of them from what is known about interatomic forces. But to investigate them experimentally, a cell was made with a buffer gas (3.1 Torr of argon) and, as expected, the line broadens as the delay increases. Fig. 12 shows the line shapes with various probe delays. Fig. 13 shows the variation of linewidth with delay time. It can be fitted from a diffusion theory which assumes that no one collision makes a large change in the velocity direction of an atom. The comparison is complicated by other sources of line broadening. It does look, however, that this method can be used to study the collision processes in the atoms.

Continuous-wave dye lasers, also exist [21]. When pumped by an argon ion laser, various dyes have given continuous laser operation from approximately 5200 Å to 7000 Å. Single-mode operation has been achieved [22]. Ultimately, it should be possible to make continuous dye lasers with extremely high stability. However, the amplification available from the dye

is less than in pulsed operation, and tuning elements must be carefully designed to have low losses. Meanwhile, pulsed tunable lasers now exist that can be made monochromatic enough to do saturation spectroscopy on any line from any gas, atomic or molecular, anywhere near the visible region. Because the pulses are so short, the states observed do not have to be long-lived states. The states may last a few nanoseconds. In all, tunable lasers have become very powerful tools with many interesting scientific applications.

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