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Tunable Coherent Optical Radiation for Instrumentation

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One afternoon some 8 years ago a colleague rushed excitedly into my laboratory. The reason for his excitement was an article entitled "Laser-pumped stimulated emission from organic dyes" by Sorokin and co-workers (1). Even at that time, it was clear that here was the potential for *tunable* laser radiation across the visible region of the spectrum. This potential for tunability was shortly thereafter demonstrated by Soffer and McFarland (2). To be sure, tunable lasers were known at that time. Pressure tuned diode lasers had been reported which could be tuned over a considerable portion of the infrared (3), but these were not simple laboratory devices and were very low in power output. The Zeeman effect had been used to tune atomic vapor lasers (4), but the amount of tunability was limited to only about a part in 10^6 in frequency. The dye laser promised broad tunability and high power in a reasonably simple laboratory device. I will admit that the developments in tunable coherent radiation sources since that afternoon have far exceeded any expectations I might have had at the time. It is my belief that the next 20 years will see a dramatic development of tunable coherent light sources and of various optical devices associated with them. Soon light will be no more difficult to work with than lower-frequency electromagnetic radiation (for instance, radio frequencies). These sources and devices will be important constituents in instrumentation for communications, spectroscopy, and spectrochemical analysis.

In this article I will review briefly some principles underlying the production of tunable coherent radiation. I will describe some specific techniques which today appear suitable for development in scientific instrumentation. I will mention some specific areas where tunable coherent radiation may be expected to play a role in scientific instrumentation.

Production of Tunable Coherent Radiation

Most sources of tunable coherent radiation consist of two essential elements. First, they must have some active medium which exhibits gain (or amplification) at optical frequencies and which provides a source of optical energy. Second, they usually include some sort of cavity which provides feedback for the control of energy flow at selected frequencies. The properties of both the active medium and the cavity determine the tuning characteristics of the radiation source (5).

For simplicity, let us consider a laser medium containing particles described in terms of two nondegenerate energy states, a and b, with energies $E_b > E_a$. Let us denote the number density of particles in states a and b by N_a and N_b, respectively. It is well known that light may be described by electric and magnetic fields oscillating at some angular frequency ω (with wavelength $\lambda = 2\pi c/n\omega$, where c is the speed of light and n is the index of refraction). This light may interact with the medium and can induce transitions between states a and b if $\omega \sim (E_b - E_a)/\hbar$, where $\hbar$ is Planck's constant divided by 2π. The inherent strength of this interaction is measured by an electric dipole matrix element between the two states, D_{ab}. The dependence on frequency is described by a line shape function, $g(\omega)$, where $\int g(\omega)d\omega = 1$ and where $g(\omega)$ usually peaks sharply at the transition frequency $\omega_{ba} \equiv (E_b - E_a)/\hbar$. For example, transitions in a molecular gas are usually dominated by the Doppler effect, for which $g(\omega) = (c/n\omega)\,(m/2\pi kT)^{1/2}\exp[-(mc^2/2kTn^2)(\omega - \omega_{ba})^2/\omega_{ba}^2]$, where m is the appropriate mass and k is Boltzmann's constant. In condensed phases or in relatively high pressure gases, the line shape function is often Lorentzian: $g(\omega) = (\pi\tau)^{-1}[\tau^{-2} + (\omega - \omega_{ab})^2]^{-1}$, where τ is some characteristic relaxation time for the system. Light (plane wave) with intensity per frequency interval S_ω^0 [erg/(sec cm^2 sec^{-1})] which is incident on an active medium of length L may either induce a→b transitions (absorption) or b→a transitions (stimulated emission). Since an induced b→a transition gives up a photon which is in phase with the incident radiation, it is possible for the light intensity to increase as the light traverses the medium. The resultant output intensity in most cases may be shown to be given by $S_\omega = S_\omega^0\exp[\gamma(\omega)L]$, where γ, the gain coefficient, is $\gamma(\omega) = (4\pi^2\omega_{ba}/3nc\hbar) \mid D_{ab} \mid^2 \times (N_b - N_a)g(\omega)$. Thus, if $N_b - N_a$ is positive, the intensity at any $\omega \sim \omega_{ba}$ grows exponentially. The output intensity and the input intensity are coherent (that is, in phase both temporally and spatially). Two features are particularly important for tunability. First, the medium will show gain in a range of frequencies about ω_{ba} determined by $g(\omega)$. Second, since the gain will peak at ω_{ba}, light which is incident at ω_{ba} is more strongly amplified than light at other frequencies. Thus, if the gain is high, considerable narrowing about ω_{ba} can take place in a single pass through the medium. Note that, without a cavity, tuning can only be achieved if the transition frequency, ω_{ba}, can be varied or if the peak frequency of the line shape function $g(\omega)$ can be altered.

Generally, the laser medium, which has optical gain near one or more transition frequencies, is placed inside a cavity consisting of mirrors, lenses, and other devices which control light. The simplest such cavity is a plane-parallel Fabry-Perot cavity consisting of two flat mirrors separated by distance l. As radiation passes back and forth between the mirrors, constructive interference will occur when the length of the cavity is an integral number of half-wavelengths—that is, when $l = q\lambda/2$ for $q = 1,2,3, \ldots$. Thus, certain frequencies (or longitudinal modes) are selected preferentially by the Fabry-Perot cavity. A detailed analysis of the coupling between the active medium and the cavity is beyond the scope of this discussion. It is clear, however, that simply adjusting the length of the Fabry-Perot cavity changes the wavelengths which are preferred by the

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cavity. If the line shape function is relatively broad, it is possible for the cavity to determine the laser wavelength. In many cases l can be adjusted so that only a single frequency satisfies $l = q\lambda/2$ with sufficient gain to overcome losses inherent in the cavity and in the medium. The single laser frequency may then be adjusted by simply changing the cavity length. In various ways, additional intracavity devices may be used to provide further wavelength discrimination. In principle, except for internal losses, tuning the laser cavity merely shapes the spectral character (frequency spread) of the laser; it does not necessarily reduce the output power. This means that the available power may be effectively channeled into the desired spectral characteristics. Considerable engineering effort may be required, however, to achieve these characteristics.

Tunable coherent radiation may also be produced by utilizing the nonlinear response of a medium to an intense coherent driving source in the following way (*5*). A macroscopic dipole moment may be induced in a medium by an electric field. We may expand the polarization of the medium (dipole moment per unit volume) in terms of the applied electric field E—that is, $P = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \ldots$, where $\chi^{(n)}$ is the nth-order susceptibility. For low fields, terms beyond the first are usually negligible. However, the radiation from a laser can provide coherent oscillating electric fields which are sufficiently intense that the higher-order terms can be quite significant. Suppose that some material is subjected to intense coherent radiation at some fixed frequency ω_p and a tunable frequency ω_t. Then through the second-order term, $\chi^{(2)}E^2$, the polarization of the material will have a component oscillating at frequency $\omega_p + \omega_t$. If the experimental conditions are chosen so that light at frequencies ω_p, ω_t, and $\omega_p + \omega_t$ can travel together in phase, then the component of polarization at frequency $\omega_p + \omega_t$ will generate radiation at that frequency. This proper choice of experimental conditions is known as phase-matching and is often difficult to achieve. It can be ingeniously accomplished in birefringent crystals of certain symmetry. For systems with inversion symmetry (such as gases) $\chi^{(2)}$ is identically zero, but tunable radiation at $2\omega_p \pm \omega_t$ may be obtained through the third-order susceptibility, $\chi^{(3)}$. There is no fundamental reason why such processes cannot be highly efficient (*6*). Thus, for example, frequency doubling ($\omega_p = \omega_t$) can occur with efficiencies in excess of 30 percent (*5*). In one case, 50 percent of the input photons at ω_t were converted to light at $2\omega_p - \omega_t$ (*7*).

The inverse of the process described above may also be used to produce tunable coherent radiation. If a material for which $P = \chi^{(1)}E + \chi^{(2)}E^2$ is subject to a driving field at frequency ω_p, oscillation will also occur at ω_i and ω_s (where $\omega_i + \omega_s = \omega_p$) when all three waves are phase-matched. This is known as parametric oscillation. An external cavity may be employed to select one particular ω_s of interest. Higher-order parametric processes are also possible, including oscillation at ω_i and ω_s where $\omega_i + \omega_s = 2\omega_p$.

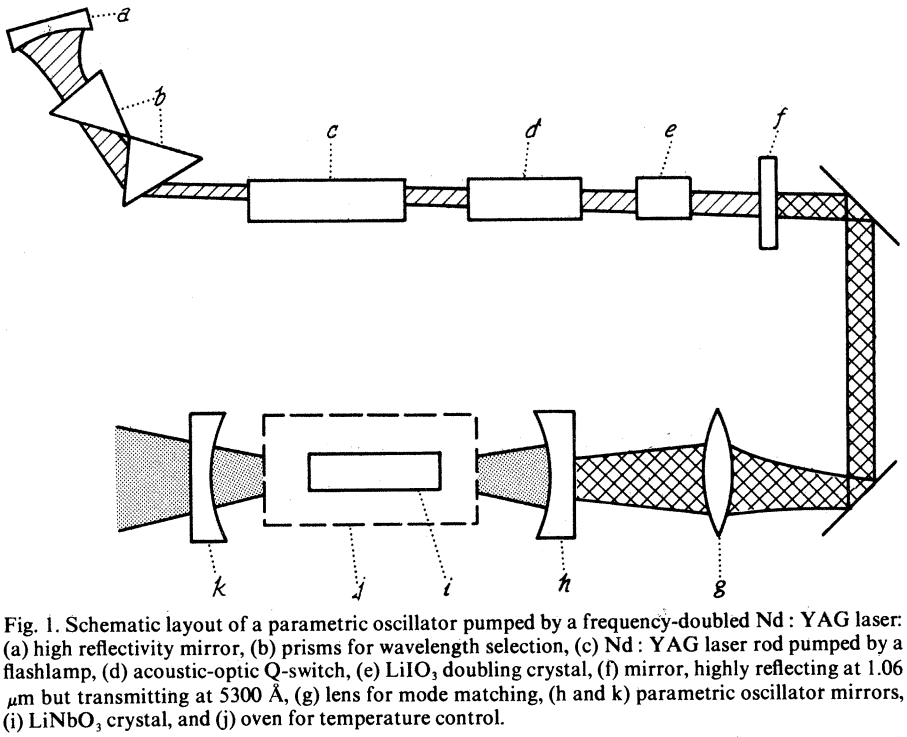

Fig. 1. Schematic layout of a parametric oscillator pumped by a frequency-doubled Nd : YAG laser: (a) high reflectivity mirror, (b) prisms for wavelength selection, (c) Nd : YAG laser rod pumped by a flashlamp, (d) acoustic-optic Q-switch, (e) $LiIO_3$ doubling crystal, (f) mirror, highly reflecting at 1.06 μm but transmitting at 5300 Å, (g) lens for mode matching, (h and k) parametric oscillator mirrors, (i) $LiNbO_3$ crystal, and (j) oven for temperature control.

Some Specific Systems for Generating Tunable Light

In the last 10 years a number of different systems have been devised for generating tunable coherent optical radiation. These systems are far too numerous and varied to discuss here. Let us briefly examine three specific systems which show promise of usefulness for scientific instrumentation in the immediate future.

Diode lasers (cavity tuned) (*8*). Semiconductors may be doped with small amounts of impurities, which may make the material either n-type, in which electrons are the principal free charge carriers, or p-type, in which "holes" are the principal charge carriers. If an electrical current is passed through a region where p-type and n-type material meet (a junction) excess electrons can be injected into the p-region and holes into the n-region. The injected electrons or holes can recombine with the free carriers, giving off radiation near frequencies corresponding to the "band gap" of the material. These frequencies usually fall in the infrared region of the spectrum. Because of the large index of refraction for most diode laser materials, a laser cavity of reasonably high reflectivity may be formed by merely polishing or cleaving the crystal. The line shape function for the electron-hole recombination emission is relatively broad. When sufficient current is passed through the junction, the gain overcomes absorption losses in the material and laser action occurs. Now for a typical crystal length of 0.1 cm and index of refraction $n \sim 4$, the spacing between longitudinal modes is $\omega_{q+1} - \omega_q = \pi c/ln \cong 2.3 \times 10^{11}$ sec^{-1} (or 1.22 cm^{-1}). Typically three or four modes oscillate simultaneously, but they may be separated with a low-resolution spectrometer. Ultimate line widths can be less than 10^7 sec^{-1} (or about 1 part in 10^8).

Tuning in diode lasers may be accomplished in a number of ways. Coarse frequency tuning can be accomplished by changing the band gap. This may be done by changing the chemical composition, by changing pressure applied to the crystal, or by applying an external magnetic field. For high-resolution tuning, the diode current may be varied. This changes the temperature and thus the index of refraction of the crystal. Since the preferred frequencies of the cavity are $\omega_p = (\pi c/nl)q$, the variation in n gives rise to variations in output frequency. Schemes such as this have been used by Nill and co-workers (*8*) to study infrared absorption spectra of several compounds of atmospheric and environmental interest, under extremely high resolution.

There is good reason to believe that tunable frequency infrared diode lasers will

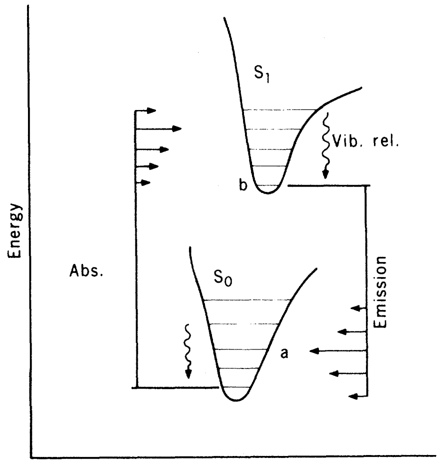

Fig. 2. Energy level diagram for typical organic laser dye.

become commercially available in the near future. Their particular advantages include relatively low cost (at least in large quantities), simple operation, narrow band width, and high reliability. There are a number of disadvantages, however. Since the band gap is fixed for a given individual semiconductor, a large number of these devices would be needed to cover a broad spectral region. Also, these lasers at the present time are usually operated at cryogenic temperatures. Although closed-cycle cryostats are readily available, the required degree of temperature control may be difficult to obtain. Finally, the tuning range for each mode is limited to ~ 1 cm^{-1}. Even for several modes, the total tuning range of each diode is small (say ~ 10 cm^{-1}). Nonetheless, diode lasers may be extremely useful, particularly for monitoring the intensity of characteristic infrared absorptions for particular molecules.

Parametric oscillator. At least one system for production of tunable coherent radiation utilizing the concept of parametric oscillation is already commercially available. Figure 1 gives a schematic description of this type of instrument. A rod of yttrium aluminum garnate (YAG) doped with neodymium ions comprises the active medium for the pump beam. The rod is excited by krypton lamps. A prism selects one of several fixed-frequency Nd laser transitions between 0.9 and 1.4 μm. A device known as a Q-switch allows the rod to store energy which may be released in a short period of time (~ 0.2 μsec). Since the efficiency of the parametric oscillator usually increases with excitation power, this is highly desirable. The Nd laser transition frequencies are doubled by a crystal with nonlinear response placed inside the laser cavity. Thus, pulses of visible radiation (530 nm) are available to excite the parametric oscillator. The latter consists simply of a $LiNbO_3$ crystal carefully temperature-controlled inside an optical cavity. The temperature of the crystal is selected so that ω_p, ω_s, and ω_i are phase-matched for the wavelengths of interest. As the crystal temperature is changed, the phase-matched output wavelengths also change, which gives rise to tunable output. Using this scheme, it is possible to obtain tunable output at wavelengths ranging from about 5400 Å to 3.7 μm with peak output powers of several hundred watts and average powers $\sim 10^{-2}$ watt. Line widths can be narrower than 0.7 cm^{-1}.

Certainly, many further developments in parametric processes can be expected. The current state of the art has been discussed by Byer (*9*), who has shown that parametric oscillator sources may be easily extended well into the infrared. Herbst *et al.* (*10*) have recently described an angle tuned parametric oscillator pumped by a Nd:YAG laser at 1.06 μm. This device can produce 10^4 ergs of infrared radiation per pulse, tunable from a wavelength of 1.5 to 4.5 μm. These power levels are sufficiently high that additional frequency doubling or other nonlinear processes can be carried out efficiently.

As a tunable source of coherent radiation, the parametric oscillator has the advantage of being a rather simple device, given the pump laser and the nonlinear crystal. It is quite reliable and generally can be expected to produce spatially well-defined beams. Also the entire infrared region of the spectrum can be covered with a relatively small number of crystals. On the other hand, nonlinear crystals of the appropriate size are difficult to grow with the requisite degree of optical purity, they may be damaged if the pump laser intensity is too high, and their temperature must be maintained to a high degree of accuracy. The pump laser is very expensive, and, finally, output at wavelengths shorter than 5300 Å is difficult to obtain directly.

Tunable dye lasers. The principles on which a tunable laser may be constructed utilizing organic dye molecules are very simple (*11*). Figure 2 gives an energy level diagram for a typical organic dye molecule. Two electronic states are shown: a ground state, denoted S_0, and an excited singlet state, denoted S_1. Since the electronic energy is a function of internuclear distance (indicated schematically by Q in Fig. 2), there are a number of discrete vibrational levels. Optical excitation of S_1 may take place into a number of excited vibrational levels. Following excitation, vibrational relaxation occurs rapidly ($\sim 10^{-11}$ second in solution). Emission may then occur to a number of excited vibrational levels of S_0. Line shape functions in solution are quite broad, so the emission spectrum is almost continuous over a wide range of frequencies. Vibrational relaxation in S_0 makes it possible to maintain $N_b > N_a$ in this system. Since the excited state lifetime is short ($\sim 10^{-8}$ second) the optical excitation must be in the form of an extremely short pulse of light, or else an extremely high pumping intensity is required to maintain $N_b > N_a$ by a sufficient amount. This has been accomplished in a number of ways.

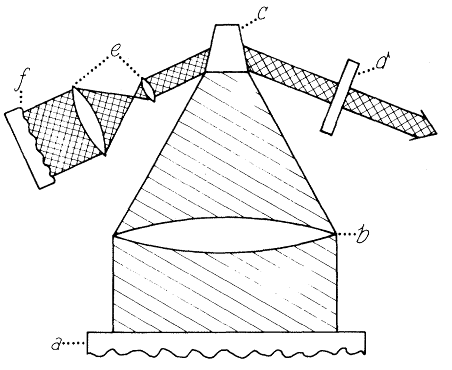

Fig. 3. Schematic for tunable dye laser pumped by a N_2 laser: (a) N_2 laser, (b) focusing lens, (c) dye cell, (d) output mirror, (e) beam expander, and (f) grating.

1) Nitrogen laser pumping. Nitrogen lasers that generate powerful (~ 100 kw or greater) pulses ($\sim 10^{-8}$ second) of ultraviolet light (near 3371 Å) have long been commercially available. Broida and Haydon (*12*) realized that these would be ideal sources for optical excitation of organic dyes and proceeded to build an extremely simple laser. Figure 3 shows a schematic version of such a laser from our laboratory. The N_2 laser beam is focused to a narrow rectangular region of a cell containing a dye solution. A telescope is used to expand the beam and to direct it to a diffraction grating, which serves as a wavelength selection device. Another mirror allows part of the laser beam to escape the cavity. Hänsch (*13*) has discussed many practical aspects of such dye laser design. Energy from the nitrogen laser can be converted to tunable radiation with efficiencies as high as 15 to 20 percent. Because of the short excitation wavelength, many different dyes can be excited in this manner, with dye laser frequencies covering the wavelength range 3,500 to 11,000 Å. Drexhage (*14*) gives an extensive list of laser dyes. Lasers of this type are now commercially available which are tunable across the wavelength range 3600 to 7500 Å with line widths as narrow as 10^{-3} Å, peak powers of ~ 10 kw, and repetition frequencies of 50 hertz. The possibility of frequency doubling extends the tuning range into the ultraviolet to 2580 Å. At the present time the cost for such a system is quite high.

2) Doubled Nd:YAG pumping. A laser

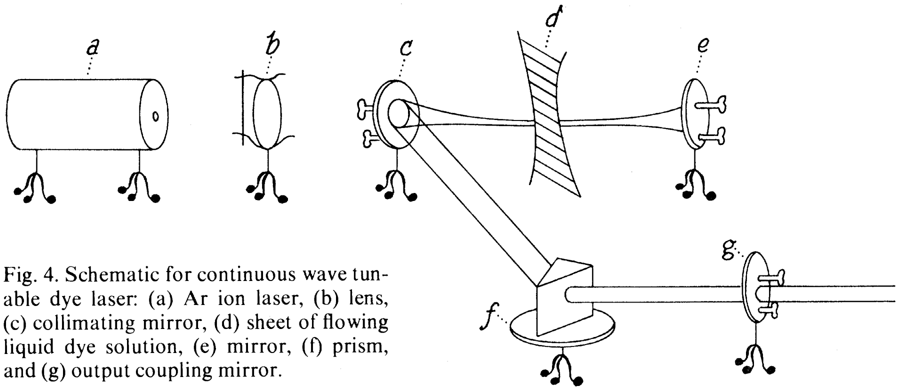

Fig. 4. Schematic for continuous wave tunable dye laser: (a) Ar ion laser, (b) lens, (c) collimating mirror, (d) sheet of flowing liquid dye solution, (e) mirror, (f) prism, and (g) output coupling mirror.

of the type used to pump a parametric oscillator is also suitable for dye laser excitation, and such an accessory is available commercially. Since the doubled Nd:YAG laser transition is near 5300 Å, only longer-wavelength dye lasers can be pumped directly (5300 to 6800 Å). Frequency doubling, however, extends the frequency range to include wavelengths from 2650 to 3400 Å. Since the excitation is in a well-defined spatial mode, the dye laser output in this case can also have well-defined spatial characteristics. Output powers and energies are of the same order as those for the N_2-laser pumped systems. Again, cost is quite high.

3) Flashlamp pumped dye lasers. From the very beginning, it was clear that flashlamp pumped dye lasers had much to offer in terms of low cost and simplicity. Thus, the original dye laser paper was accompanied by a short communication in which Sorokin and Lankard (*15*) described a flashlamp pumped dye laser system. A detailed description appeared later (*16*). Although such lasers can be built simply and cheaply, considerable engineering is required for accurate and reliable operation. Several versions are commercially available, ranging in price from $3,000 to $15,000. One version provides peak powers of 1 to 8 kw with pulse widths of 0.5 μsec, repetition frequencies of 30 hertz, and band widths of the order of 3 cm^{-1} (or 0.1 cm^{-1} with some loss of power). The advantages of flashlamp pumped lasers include simplicity and lower cost, but they do have some drawbacks. Generally, a considerable amount of energy is absorbed by the dye. This gives rise to heating of the solution, which produces temporal and spatial inhomogeneities in the active medium, and photochemical degradation of the dye. Also uniform excitation is difficult to achieve, which leads to a number of problems concerning reproducibility of intensity and wavelength.

Continuous wave dye lasers. All the dye lasers described above operate in a pulsed mode because of the short lifetime of the excited state. However, if the exciting intensity is sufficiently high, continuous wave operation is possible. This may be accomplished by focusing an Ar ion laser beam to a very small spot, as first demonstrated by Peterson *et al.* in 1970 (*17*). Figure 4 shows a typical experimental arrangement. With pumping powers of 10 watts, one can expect average output powers of ~ 1 watt with extremely narrow line widths. Since pumping is usually at 5145 Å, output is restricted to longer wavelengths, although frequency doubling can provide intense ultraviolet output. Several versions are commercially available, but the high cost and limited lifetime of the Ar ion laser are distinct disadvantages.

A principal advantage of the tunable dye laser, whether flashlamp pumped or laser pumped, is its inherent simplicity. Furthermore, an extremely wide range of wavelengths is available, covering the entire visible and including the near ultraviolet and the near infrared. With flashlamp pumping, in particular, large output energies may be produced quite cheaply. The liquid medium entails a number of problems concerning index of refraction gradients and thermal gradients. Also the dyes are subject to some photochemical degradation. These problems are more severe with flashlamp pumping than with laser pumping. Nonetheless, the dye laser, in one form or another, is an extremely good candidate for tomorrow's universal light source.

Applications

When accurate frequency control is combined with the other unique properties of coherent radiation, an extremely powerful tool for all kinds of scientific investigation results. Where may we expect these developments to appear in scientific instrumentation? Many potential applications are evident in the areas of spectroscopy, photophysics and photochemistry, and spectrochemical analysis. I will point out only a few particular applications for each of these areas.

1) *Spectroscopy.* In spectroscopy, the frequencies of absorption of light by an atomic or molecular system are studied and related to the energy levels of the system. For spectroscopists, then, tunable coherent radiation is the ultimate light source. Among the particular advantages of the laser source over conventional sources is the high resolution available, sufficient to resolve virtually any absorption feature. Furthermore, the high intensity allows accurate determination of very strong absorption coefficients. It also allows the use of novel schemes to detect small amounts of absorption—for instance, fluorescence detection or detection of ions. With tunable coherent sources spectrometer design becomes quite simple, since only the source, sample, light detector, and detection electronics are required. Examples of absorption spectroscopy carried out with tunable coherent sources are numerous. Pruett and Zare (*18*), for instance, were able to study weak optical absorptions in BaO, utilizing fluorescence detection. We may certainly expect the development of laser-equipped visible and infrared spectrometers, although the cost for some time may exceed that of conventional instruments.

Tunable lasers may also be expected to be of major importance in resonance Raman spectroscopy. The basic idea of this technique is that with excitation near some electronic absorption frequency, the Raman scattering is enhanced for certain vibrational modes that are associated with the chromophore responsible for the absorption. This can result in a considerably simplified spectrum for very large molecules, particularly ones of biological interest. Specific application to biological systems has been pointed out by Spiro (*19*). A resonance Raman spectrometer with tunable laser source for commercial production is certainly quite feasible today.

The high intensity of laser sources make them ideal for two-photon absorption experiments. It is well known that many transitions which are forbidden in normal spectroscopy become allowed when absorption of two (or more) photons is considered. McClain (*20*) has demonstrated that tunable laser spectroscopy involving absorption of two visible photons can be accomplished and that it can provide insight into the electronic structure of molecules. The advent of tunable lasers has already revolutionized this field. In other experiments, Oka (*21*) has used fixed infrared laser and variable microwave frequencies to carry out high-resolution two-photon infrared spectroscopy.

Coherence makes possible an additional type of spectroscopy involving the nonlinear response of a medium to oscillating electric fields. The susceptibilities, $\chi^{(n)}$, involve terms that go through resonances when appropriate sums and differences of the frequencies of applied electric fields correspond to differences between energy levels of the medium. When phase-matched conditions are met, resonances will occur in the intensity of light generated at appropriate sum and difference frequencies. Armstrong and Wynn (*22*) have used this idea to examine autoionizing energy levels of Sr vapor. Such ideas could be extended to molecules. In somewhat related experiments Begley *et al.* (*23*) have observed resonances in χ which correspond to vibrational levels of the molecule under investigation. They call this technique coherent anti-Stokes Raman spectroscopy (CARS). It has a number of advantages over normal Raman spectroscopy, particularly where fluorescence and other forms of background radiation may interfere. This may provide an extremely effective technique for identifying and monitoring the concentration of certain components in flames.

Finally, it should be pointed out that tunable coherent radiation, particularly in the ultraviolet and vacuum ultraviolet, should make possible many forms of photoionization spectroscopy. Lineberger and co-workers have measured the intensity of photoelectrons emitted from negative ions as a function of applied wavelength (*24*). In addition, several photoionization spectra have been obtained with dye lasers (*25*). It soon may be possible to produce molecular photoionization spectra on a relatively routine basis.

2) *Photophysics and photochemistry.* The monochromaticity of the light sources described here as well as the ease of time modulation makes them ideally suited for many types of molecular relaxation studies. With a tunable source specified energy levels of some molecular system can be optically excited. Various properties of the system may then be monitored as a function of time. These properties might include such things as fluorescence from various states, temperature, and magnetic moment. For example, we have used tunable dye lasers to excite small gas molecules (such as propynal or glyoxal) to specified vibrational levels of excited electronic states (*26*). The time dependence of the fluorescence and phosphorescence has enabled us to map out how the energy-flow paths depend on initial state. We have also applied similar techniques to some rare earth and transition metal complexes. Given the tunable laser source, the instrumentation for such experiments is extremely simple. Many relaxation processes in condensed media occur on picosecond (10^{-12} second) time scales. Examples include orientational relaxation, vibrational relaxation, and electronic relaxation. Studies of picosecond relaxation have been carried out by Eisenthal (*27*), Netzel *et al.* (*28*), and Kaiser and co-workers (*29*), using fixed frequency sources. Tunable picosecond pulses offer the possibility of dramatically extending the applicability of picosecond relaxation studies.

It is easily verified that 1 watt of continuous radiation at 600 nm corresponds to about 10^{22} photons per hour, or 1.5×10^{-2} mole of photons per hour. If each photon is used to produce a photochemical product, laboratory quantities may be readily prepared. Now, since the photochemical pathways can be wavelength dependent in many cases, a tunable laser source makes possible selective photochemistry. Furthermore, examination of the photochemical products as a function of incident wavelength can shed considerable light on the nature of the photochemical processes involved. It is significant that very little is known at present about the wavelength dependence of photochemical reactions, even in solution.

Of particular importance among potential photochemical applications of tunable lasers is the possible production of isotopically selected products. The basic idea is simple. Molecular and atomic spectra contain numerous examples of isotope effects; that is, molecules composed of different nuclear isotopes absorb light at different frequencies. A laser tuned to the transition frequency of a particular isotope will excite primarily that one. A subsequent chemical or physical process sensitive only to excited molecules can be used to isolate the selected isotope. Some specific ways of doing this have been described by Moore (*30*) and Letokov (*31*). These methods could, in principle, provide enriched fissionable material far less expensively than gaseous diffusion. They also could provide inexpensive isotopes for all types of chemical labeling and for radioactive tracers.

3) *Spectrochemical analysis.* Perhaps the greatest potential for tunable lasers in scientific instrumentation is in the area of spectrochemical analysis. High-intensity light means that signals can be large; measurements can be made rapidly. Monochromaticity gives high selectivity. Programmability of wavelength means that information can be obtained efficiently. Recently, using a tunable dye laser, Fairbank *et al.* (*32*) demonstrated the detection of Na atoms at concentrations of only 100 atoms per cubic centimeter! This certainly suggests a general scheme for the analytical determination of atomic composition. A vaporized sample could be subjected to laser radiation tuned to a characteristic atomic absorption. Fluorescence would then indicate quantitatively the concentration of the appropriate atomic species. This method could be orders of magnitude more sensitive than other techniques. This same basic idea has already been used by Zare and Dagdigian (*33*) to detect low concentrations of chemical reaction products in molecular beams. Tunable lasers will be useful for detection of pollutants and in other forms of concentration monitoring. In particular, both laser-induced fluorescence and resonant Raman scattering have been proposed for remote detection.

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