Tunable Lasers and their Application in Analytical Chemistry

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TUNABLE LASERS AND THEIR APPLICATION
IN ANALYTICAL CHEMISTRY

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I. INTRODUCTION TO
LASER SPECTROSCOPY

The laser, as a light source, has had a revolutionary impact in chemical and physical research involving optics and spectroscopy. One simple reason for this is that the source spectral brightness — that is, the amount of energy delivered per unit area and frequency interval — associated with a laser can be 10 or more orders of magnitude greater than that associated with conventional light sources. Thus, the response of a system being probed by a laser is enormously enhanced, making experiments that much more sensitive. At least as significant is the fact that the laser is a *coherent* radiation source, which can be tuned and modulated. This permits the use of coherent detection techniques, similar to those used in radiofrequency and microwave spectroscopy, which further increase sensitivity.

In this review, we shall consider the impact that laser techniques might have in a particular area, that of chemical analysis. Descriptions of the various types of laser spectroscopy can be found in several books and articles,[1-4] but analytical applications have not yet been considered in the same

way. Particular emphasis will be placed on the advantages of using frequency-tunable sources, and dye solution lasers will be considered as the outstanding example of this type of laser. First, though, we shall rehearse some general considerations of the types of spectroscopy that can be carried out with lasers, and the ultimate sensitivity of which these methods may be capable.

A. Experimental Methods

Three types of experimental methods we shall consider in this review are absorption, scattering, and heterodyne detection. For further details, see Reference 2.

Absorption — The simplest spectroscopic method that can be used to measure the concentration of some species is direct absorption based on Beer's Law. The advantage that lasers bring to this method is primarily the high resolution that can be attained; source bandwidths of 10 to 100 kHz ($\sim 10^{-6}$ cm^{-1}) are not untypical in the visible and mid-infrared regions of the spectrum. Since a laser beam can also be propagated over quite long distances with very little divergence, it is ideally suited to remote-sensing applications, that is, direct absorption through long paths in the atmos-

phere. The high intensities available from lasers are often sufficient to drive a system into saturation, which makes possible such non-linear absorption effects as Lamb Dip and double resonance.

Scattering — Several different types of phenomena may be distinguished, namely Raman effect (inelastic light scattering), Rayleigh effect (elastic light scattering), and fluorescence (absorption and reemission involving the excitation of a real intermediate state). Of these, Raman and fluorescence scattering have had the most use in analytical procedures. The high power available from lasers increases the signal levels in these types of experiments, and the ability to produce short (down to 10^{-12} sec) excitation pulses permits the use of time-gated detection schemes. At very high power levels, such nonlinear effects as two-photon fluorescence and stimulated Raman scattering are possible.

Heterodyne Detection — An additional way in which lasers can be used, one that is especially suited for remote-sensing and environmental-monitoring applications, is as a local oscillator heterodyned with weak emission signals from remote sources. This is the same principle that is employed in a radio receiver to amplify weak broadcast signals.

B. Ultimate Sensitivity

The principal question of interest to an analytical chemist, with regard to the various methods described above, is the sensitivity limit, or minimum detectable concentration of molecules in a sample, that can be achieved with each. This problem has been considered by Shimoda,[5] and it will be instructive to state his results for two particular cases: direct-absorption spectroscopy, and nonlinear (two-photon) spectroscopy. These are, of course, the ideal limits for the best possible experimental situations.

In general, the greatest sensitivity is obtained by coherent detection of the response of the system being investigated to modulation of the light. With lasers, this can be done either by chopping or by direct frequency modulation of the radiation source itself. The minimum detectable change in power is that which gives a signal equal to the intrinsic noise of the radiation detector; its magnitude depends on the type of detection used, and thus on the wavelength range of interest. For the infrared, this minimum power is given by

$$P_n = \sqrt{A\Delta f/D^*} \tag{1.1}$$

where A is the area of the detector, Δf the bandwidth of the frequency-selective amplifier, and D^* the characteristic detectivity of the detector. Typically, $A \sim 0.1$ cm^2, $\Delta f \sim 1$ to 10 Hz, and $D^* \sim 10^9$ to 10^{10} W^{-1} cm Hz$^{\frac{1}{2}}$; thus, $P_n \sim 10^{-9}$ to 10^{-10} W. For a photoelectric detector,

$$P_n = h\nu/4\eta\Delta t \tag{1.2}$$

where ν is the frequency of the light, η the quantum efficiency of the photocathode, and Δt the counting interval. Typically, $\nu \sim 10^{15}$ Hz ($\lambda \sim 3000$ Å), $\eta \sim 0.25$, and $\Delta t \sim 1$ to 10 sec. This gives $P_n \sim 10^{-19}$ W, which corresponds to single-quantum detection.

The sensitivity limit for an ideal direct absorption experiment can be evaluated in either the Doppler-broadened (low-pressure) or collision broadened (high-pressure) limit. In the Doppler limit,

$$N_{min} = \frac{8v}{c} \left(\frac{2\epsilon_0 c\tau A P_n}{\pi |\mu_{ij}|^2 \gamma} \right)^{\frac{1}{2}} \tag{1.3}$$

where v is the rms thermal velocity, c the speed of light, ϵ_0 the permittivity of vacuum, τ the lifetime of the upper level of the transition, γ the homogeneous width of the line, and μ_{ij} the transition dipole moment. Typical values of these parameters are

$v \sim 3 \times 10^4$ cm sec^{-1}
$\tau = \gamma^{-1} \sim 10^{-8}$ sec
$\mu_{ij} \sim 3.5 \times 10^{-10}$ coulumb-meters (m.k.s.) = 1 Debye (d).

With $A \sim 0.1$ cm^2 and $P_n \sim 10^{-19}$ W, as before, this gives a relationship

$$N_{min} d \sim 10^3 \tag{1.4}$$

where d is the transition moment in Debye units. For $d \sim 1$, $N_{min} \sim 10^3$, corresponding to 3 parts in 10^{14} of 1 cm^3 of gas at a pressure of 1 torr.

In the pressure-broadened limit,

$$\frac{(N_i \cdot N_j)_{min}}{N} = \frac{0.15}{d^2} \frac{\lambda}{L} \left(\frac{P_n}{P} \right)^{\frac{1}{2}} \tag{1.5}$$

where N_i and N_j are the partial densities of the molecules in the quantum states participating in the transition, N is the total gas density, λ the

wavelength of the light, L the length of the absorption cell, and P the net laser power. With d ~ 0.3, $\lambda \sim 0.5$ μm, L = 25 cm, $P_n \sim 10^{-19}$ W, and P ~ 0.01 W, we again obtain $(N_i - N_j)/N \sim 1$ part in 10^{14}.

These astoundingly low sensitivity limits must be tempered by the fact that, of all the molecules of a given chemical species, only a small fraction will be in the one quantum state that is in resonance with the particular laser frequency. This fraction is often of the order of 10^{-4}, so that the practical sensitivity limit for a given species will be a few parts in 10^{10}, or less than one part per billion (1 ppb). This sensitivity has, in fact, been achieved in a number of the examples to be considered in Section III.

For the ideal fluorescence detection scheme, the lower limit of detectivity is

$$N_{min} = \frac{32(2\pi)^{3/2} u \Delta F \tau}{\Omega_F \eta \eta_F \gamma \lambda} \tag{1.6}$$

The undefined quantities in Equation 1.6 are Ω_F, solid angle from which the fluorescence is collected, and η_F, the fluorescence quantum yield. Ω_F can be of the order of 0.1 sr if the fluorescence is simply imaged on a detector, perhaps through a filter, but can go down to 10^{-3} sr or less if an analyzing monochromator is employed. If we take the values,

$u \sim 10^4$ cm sec^{-1}
$\Delta F \sim 1$ Hz
$\tau \sim 10^{-6}$ sec
$\Omega_F \sim 0.1$ sr
$\eta \sim 0.25$
$\eta_F \sim 0.05$
$\gamma \sim 10^8$ sec^{-1}
$\lambda \sim 10^{-4}$ cm,

we find $N_{min} \sim 10^2$ particles, or 3 parts in 10^{15} of 1 cm^3 of gas at 1 torr. In actual experimental situations, sensitivity limits of $N_{min} \sim 10^4$ to 10^5 particles have been achieved (see Section III.C.3).

II.. VARIETIES OF TUNABLE LASERS

The various techniques described in the previous section are all rendered much more useful if the laser source is tunable over a wide wavelength range, so that the laser can be tuned to coincide with a transition of interest. Tunable devices that are now available include solid-state lasers and frequency converters in the infrared portion of the spectrum, and organic dye solution lasers in the visible. The latter will be described in some detail below.

A. Solid-State Infrared Devices

Tunable infrared devices have been described in reviews by Mooradian and Nill.[6] The most important classes of devices are the following:

(1) Optical parametric oscillators are crystals (LiNbO$_3$, etc.) that convert pump light (typically frequency-doubled Nd:YAG at 5320 Å) to infrared and long-wave visible photons. Tuning is achieved by varying the temperature, and thus the refractive index, of the material. The available range is 0.7 to 10 μm, and a linewidth of 0.001 cm^{-1} can be obtained with frequency-narrowing etalons.

(2) Spin-flip Raman lasers use a CO or CO$_2$ laser to produce stimulated Raman scattering from Zeeman levels in a semiconductor, such as InSb. Tuning is accomplished by varying the Zeeman energy spacing with a magnetic field. Wavelengths from 5 to 6 μm (CO pump) and 9 to 14 μm (CO$_2$ pump) can be obtained.

(3) Semiconductor diode lasers operate on the basis of recombination radiation from DC-pumped materials, such as Pb$_{0.88}$Sn$_{0.12}$Te or PbS$_{0.74}$Se$_{0.26}$. The composition of the material determines the region in which a semiconductor laser operates; fine tuning results from varying the temperature of the crystal by changing the current passing through it. These materials operate only below 60 to 70 K and often show "gaps" in their tuning ranges. The radiation produced has a bandwidth of 10^{-6} cm^{-1} ($\sim$30 kHz).

B. Nonlinear Mixing Techniques

The tuning range of a laser can be considerably extended by the use of optical mixing. If the beams from an intense fixed-frequency source, such as a ruby or Nd laser, and from a tunable source, such as a dye laser, are combined in a suitable nonlinear bifringent crystal, such as KH$_2$PO$_4$ (KDP), LiNbO$_3$, or Ba$_2$NaNb$_5$O$_{15}$ ("banana"), then sum-frequencies in the ultraviolet and difference-frequencies in the infrared can be obtained. Optical mixing techniques are being extended into the vacuum-ultraviolet region with the

use of metal atom vapors as nonlinear elements. The basic tunable device in these schemes, however, is a dye solution laser, and we shall proceed to consider this class of lasers in more detail in the following section.

C. Organic Dye Solution Lasers

The most important class of tunable lasers for analytical applications is that of the optically pumped organic dye solution lasers. These lasers were discovered quite by accident in 1966, in the course of investigations of the saturable absorption and resonant Raman characteristics of various dyes. Since that time, hundreds of different dye laser configurations have been developed.

These lasers have a unique combination of characteristics that make them especially valuable for spectroscopic applications. The range of possible dyes is so broad that laser action can be obtained anywhere from the near UV to the near IR portions of the spectrum, from 340 to 1,200 nm. Each dye has a broad, continuous-gain bandwidth, over which continuous tuning may be achieved. Since this bandwidth generally has an appreciable homogeneous component, frequency-narrowing techniques can be used quite effectively to reduce the linewidth at any given wavelength to the order of $\Delta\lambda/\lambda \sim 10^{-10}$. Alternatively, the entire bandwidth can be employed to mode-lock the dye, thus producing pulses of the order of 10^{-11} sec duration. Many of the dyes have sufficiently high output power to permit the use of frequency-doubling, thus extending the effective tuning range into the ultraviolet (250 to 350 nm). A comprehensive discussion of dye lasers and their applications may be found in the recent book by Schäfer[7], and in review articles by Webb.[8]

1. Types of Dyes

Almost any type of colored organic species, it seems, can be made into a laser if it possesses the following characteristics: a high quantum yield of fluorescence; an appreciable Stokes shift between absorption and emission bands; and low losses resulting from triplet-triplet absorption. The structures of some representative laser dyes are shown in Figure 1. Other important classes of laser dyes are the phenyloxazoles and related organic scintillators, condensed hydrocarbons, such as anthracene and perylene, sodium fluorescein, and acridine red. Even natural products, such as chlorophyll, have shown laser action.[9]

The dyes are usually employed as a dilute (10^{-5} to $10^{-3} M$) solution in a suitable transparent host medium. This is most often a solvent such as methanol, water, ethylene glycol, or dimethyl sulfoxide. However, dye lasers have also been constructed in such forms as a solid solution in polymethyl methacrylate, a "semisolid" solution in edible gelatin,[10] or in the vapor phase.[11]

2. Pumping Methods

The only method that has been employed to date for the pumping of dye lasers is direct optical excitation of the first excited singlet state of the dye. A variety of pumping sources can be used, depending on the absorption band of the dye being used. Q-switched pulses from ruby (6,943 Å) or from frequency-doubled neodymium (5,310 Å) are effective for the longer-wavelength dyes. Direct flashlamp excitation is feasible if the rise time of the photoflash is short enough (0.3 μsec or less); flashlamps constructed coaxially with the dye cell have been found to be most efficient in coupling light energy into the laser medium. The most general pumping source is the nitrogen laser at 3,371 Å, since most dyes have appreciable absorption in this part of the ultraviolet spectrum. The only disadvantage of this pumping source is that the N_2 laser pulses themselves are very short (2 to 5 nsec) in duration and deliver small amounts of energy per pulse. Recent developments in N_2 lasers, however, have seen this pulse length increased to 0.5 μsec or more,[12] and this should be very useful for pumping dye lasers.

All the sources cited so far are pulsed in nature. Continuous-wave (c.w.) dye laser operation can be obtained by pumping with argon or krypton lasers at either visible (4,880Å, 5,145Å) or ultraviolet (3,638Å) wavelengths. A typical c.w. cavity configuration is illustrated in Figure 2.

The efficiency of conversion of pump light to laser output ranges from as much as 20% for c.w. pumping to over 50% for pulsed-laser pumping; it is appreciably less for flashlamp pumping. The overall efficiency of these devices is still low, however, due to the low electrical efficiency of ruby, Nd, Ar ion, and N_2 lasers themselves.

3. Frequency-Narrowing Methods

One of the principal advantages of the dye laser is the extremely narrow bandwidth that can be obtained, along with the wide range over which the output can be tuned. In order to achieve this
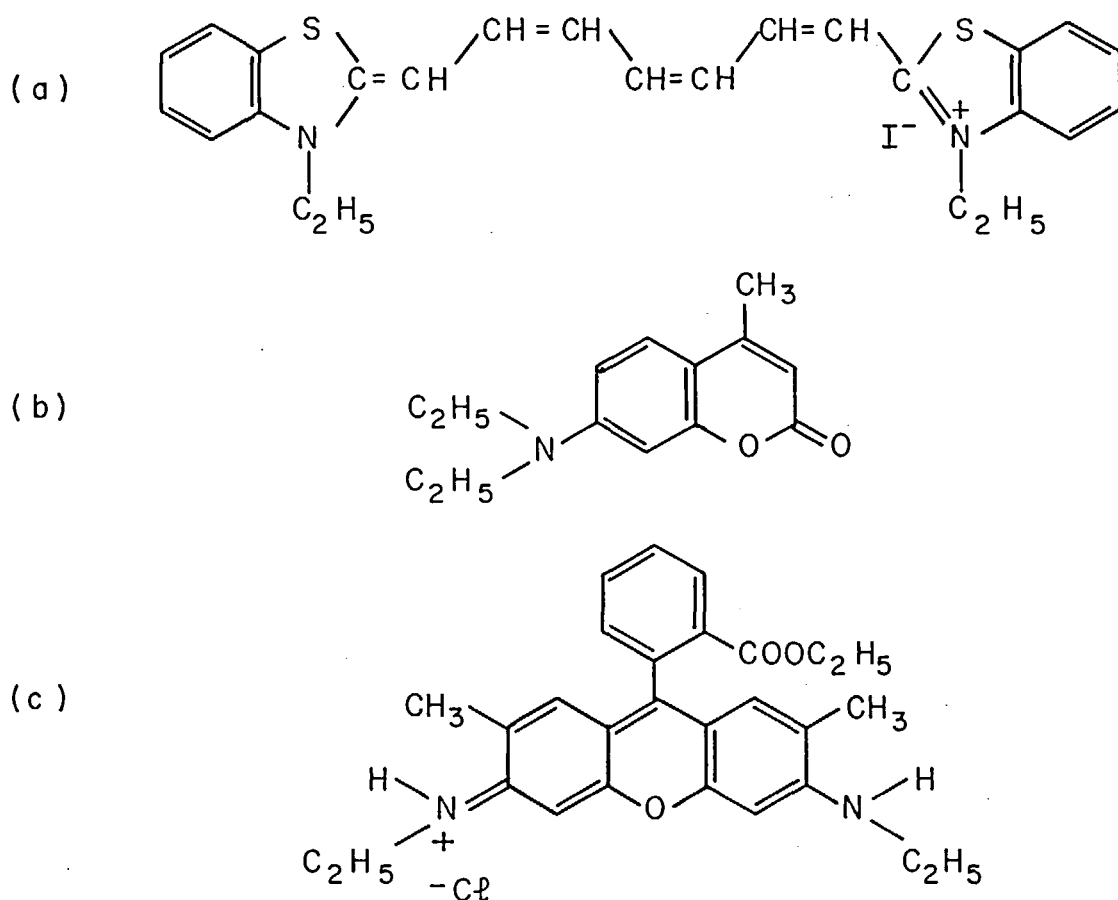
FIGURE 1. Structures of representative laser dyes. (a) 3,3'-diethylthiatricarbocyanine iodide (cyanine type), $\lambda_{laser} \sim$ 8,000 Å. (b) 7-diethylamino-4-methylcoumarin (coumarin type), $\lambda_{laser} \sim 4,700$ Å. (c) rhodamine 6G (xanthene type), $\lambda_{laser} \sim 6,000$ Å.

resolution, a variety of frequency-selective elements must be incorporated in the cavity. A diffraction grating, a train of prisms, or a birefringent Lyot filter (such as shown in Figure 2) is most commonly used for gross wavelength selection. For narrow-band (less than 1 cm^{-1}) operation, additional frequency discrimination is required. This most commonly takes the form of one or more etalons, or narrow-gap Fabry-Perot interferometers, placed inside the cavity. Another design makes use of a short subsidiary cavity coupled to the main laser cavity, known as a Fox-Smith mode selector. Tuning of these devices can be accomplished by either tilting the etalon with respect to the optical axis of the cavity, varying its length with a piezoelectrically controlled translator, or varying the refractive index inside the interferometer by changing the air pressure inside a sealed enclosure. A spectral width of 200 kHz has been achieved in a c.w. dye laser by means of such devices, with a long-term stability of 6 parts in 10^{13}.[14]

4. Summary of Operating Parameters

The typical performance characteristics of a number of commercially available dye lasers are summarized in Table 1. The c.w. dye lasers are capable of delivering up to 1 W of power. N$_2$-laser-pumped dyes have a tuning range extending into the near UV, high peak powers, but rather low average powers. Flashlamp-pumped dyes have the highest available pulse energies, but a limited tuning range. The tuning ranges and output powers available from a typical c.w. dye laser are shown in Figure 3.
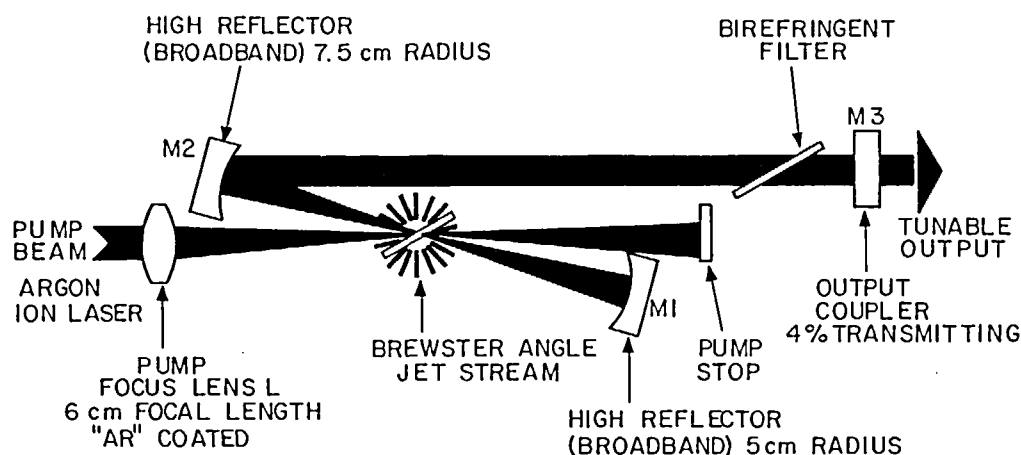
FIGURE 2. Schematic diagram of the optical layout of a confocal-cavity c.w. dye laser pumped by an argon-ion laser. (From Jarrett, S. M., *Electro Opt. Syst. Des.*, p. 24, September 1973. With permission.)

TABLE 1

Performance Characteristics of Commercially Available Dye Lasers

Manufacturer	Model	Wavelength range, A	Resolution (without etalons), A	Output Power Peak	Output Power Average or c.w.	Pumping source
Spectra-Physics Mountain View, Calif.	375	4,300–8,000	0.1		0.1–0.9 W c.w.	Ar ion
Coherent Radiation Palo Alto, Calif.	490	4,200–7,900	0.5		0.1–0.9 W c.w.	Ar ion
Laser Energy Rochester, N.Y.	337	3,700–6,500	1	5 kW	4 mW	N_2
AVCO Everett, Mass.	Dial-a-Line	3,600–6,700	2–5	10 kW	1 mW	N_2
Molectron Sunnyvale, Calif.	DL series	3,600–7,400	0.2	20–100 kW	500 mW	N_2
Chromatix Mountain View, Calif.	1050	5,300–6,800 2,650–3,400 (frequency-doubled)	0.3 0.3	0.1–0.7 kW 30–200 W	2–25 mW 0.5–5 mW	Doubled Nd:YAG Doubled Nd:YAG
Chromatix Mountain View, Calif.	CMX-4	4,400–7,000[a] 2,650–3,500 (frequency-doubled)	1 1	1–6 kW 50–400 W	20–200 mW 1–12 mW	Flashlamp Flashlamp
Candela Newton, Mass.	SLL-625	4,200–6,200		200 kW	200 mW	Flashlamp
Electro-Photonics Belfast, Northern Ireland	23	4,400–6,900	1	5–12 kW	50 mW	Flashlamp

[a] A parametric oscillator accessory is now available for the CMX-4, which extends the tuning range out to 2.6 μm.
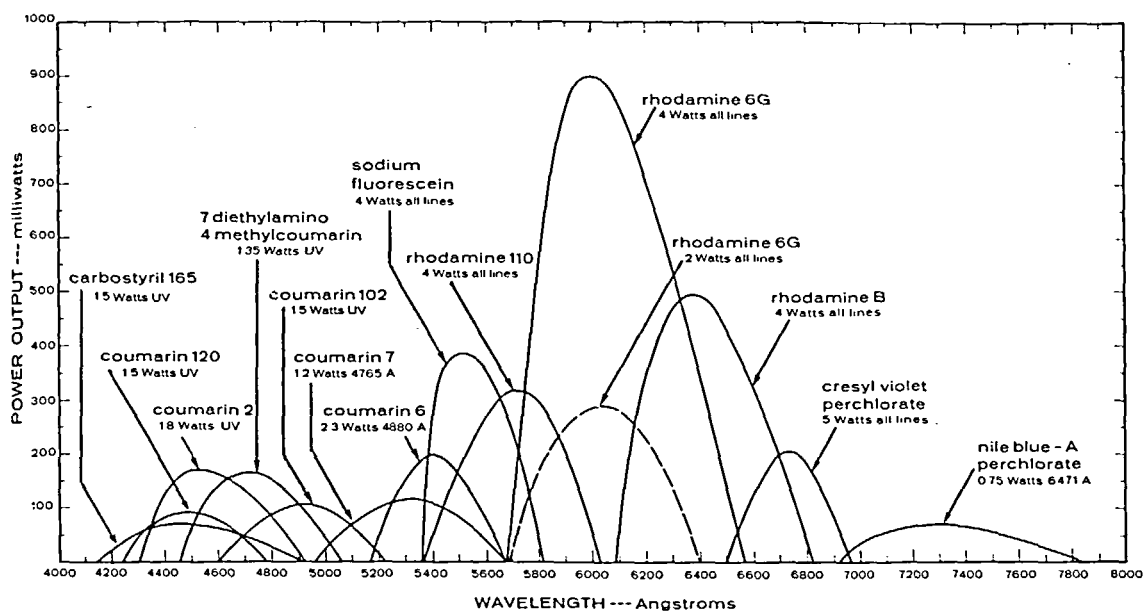
FIGURE 3. Output wavelengths and powers available from a commercial c.w. dye laser. The argon pumping radiation employed is indicated for each dye. (From Yarborough, J. M., *Appl. Phys. Lett.*, 24, 629, 1974. With permission.)

III. ANALYTICAL APPLICATIONS

A. Laser Microprobe Analysis

The first use of any laser device in analytical chemistry was in microprobe analysis. It was found convenient to use the energy of a focused pulsed laser to simultaneously vaporize and excite small regions on the surface of a sample, following which conventional emission-spectrographic analysis could be used to determine the concentrations of various metallic elements in the ejected plume. Tunable lasers offer no advantage for this type of analysis, and we shall not consider the subject further, except to cite some representative literature references in this area.[16-23]

B. Remote Sensing

One type of analytical procedure made possible by lasers is that of remote sensing. Since a laser beam can be made to propagate with very little divergence over long distances and can be refocused on a detector with conventional optics, the idea of using such a device as an optical probe has been suggested a number of times. An obvious application is the determination of trace amounts of absorbing gases in atmospheric-pollution monitoring.[24-26] Most actual prototypes of such monitoring systems to date have used fixed-

frequency laser sources, but the potential advantages of tunable sources are clear.

There have been two basic approaches to the use of lasers in remote sensing and environmental monitoring. One approach uses direct absorption over a long path through the atmosphere; this is simple, direct, and sensitive, but requires the use of remote retroreflection to return the beam to a central monitoring station. The other approach makes use of backscattered light, resulting from either Raman effect, fluorescence, or Rayleigh and Mie scattering in the atmosphere. The efficiencies and sensitivities of the various methods have been compared,[27,28] and long-path absorption was found to have the highest overall sensitivity.

1. Long-Path Absorption Monitoring

Most of the long-path absorption monitoring schemes described to date have made use of fixed-frequency rather than of tunable lasers, taking advantage of near-coincidences between available laser lines and molecular absorption features in the species being detected. For example, Menzies[29] calculated the sensitivities achievable in direct absorption of CO and frequency-doubled CO_2 laser lines by such gases as NO, NO_2, SO_2, and CO, and found a lower limit of the order of one part per million (1ppm) of a standard atmosphere. Kreuzer et al.[30] have been

able to lower these sensitivity limits nearly three orders of magnitude by the use of a spectrophone, or optoacoustic detection, which is described in more detail in Section III.C.4. Their results are shown in Table 2.

A somewhat different approach was taken by Menzies and Shumate,[31] who assessed the sensitivity limits of using a laser as local oscillator to heterodyne with the thermal emission of trace atmospheric components at remote distances. They found limits of the order of 1 ppm for NO and SO_2, and of the order of 1 ppb for O_3, C_2H_4, and NH_3.

Recently, Green and Steinfeld[32] have been investigating the more complex problem of direct-absorption sensitivity limits in mixtures of trace components in a contaminated atmosphere. The

mixture is probed at a series of fixed frequencies from a multiline gas laser, and the resulting set of absorbances is reduced to the concentrations of the individual components by solving a set of simultaneous equations, using known absorption coefficients for the pure components. The minimum detectable concentrations of some typical species, which can be determined with a relative accuracy of ±20% in a 10-m absorption path, are given in Table 3. The values in this table are of interest because they are all below the limits recommended by both NIOSH and the NAS-NRC Committee on Toxicity Standards for short-term (1-hr) exposure to these gases. Several are also below the long-term (6-month) exposure limits. The exception is vinyl chloride, for which a zero exposure level is being considered; however, laser-

TABLE 2

Noise-limited Sensitivities for Detecting Pollutant Gases

Gas	Sensitivity, ppb	Laser	Infrared source transition	Wavelength, μm
Ammonia	0.4	CO	$P_{19-18}(15)$	6.1493
Benzene	3	CO_2	$00^\circ 1-02^\circ 0$ P(30)	9.6392
1,3-Butadiene	1	CO	$P_{20-19}(13)$	6.2153
1,3-Butadiene	2	CO_2	$00^\circ 1-10^\circ 0$ P(30)	10.6964
1-Butene	2	CO	$P_{19-18}(9)$	6.0685
1-Butene	2	CO_2	$00^\circ 1-10^\circ 0$ P(38)	10.7874
Ethylene	0.2	CO_2	$00^\circ 1-10^\circ 0$ P(14)	10.5321
Methanol	0.3	CO_2	$00^\circ 1-02^\circ 0$ P(34)	9.6760
Nitric oxide	0.4	CO	$P_{8-7}(11)$	5.2148
Nitrogen dioxide	0.1	CO	$P_{20-19}(14)$	6.2293
Propylene	3	CO	$P_{19-18}(9)$	6.0685
Trichloroethylene	0.7	CO_2	$00^\circ 1-10^\circ 0$ P(24)	10.6321
Water	14	CO	$P_{17-16}(13)$	5.9417

From Kreuzer, L. B., Kenyon, N. D., and Patel, C. K. N., *Science*, 177, 347, 1972. With permission.

TABLE 3

Sensitivity and Exposure Limits for Atmospheric Contamination

Gas	Minimum detectable concentration, ppm	Recommended exposure limits, ppm	
		Short-term	Long-term
Freon-12	1.1	5,000	100
Vinyl chloride	6.4	–	–
Cyclohexane	126.0	300	60
Benzene	25.0	100	1
Isopropyl alcohol	14.0	200	40
Ethyl acetate	4.2	300	50
Methyl chloroform	5.3	300	50

absorption spectroscopy is so sensitive and specific for this material that a monitoring system for vinyl chloride, based on infrared laser detection techniques, would appear to be highly attractive.

The techniques described so far all make use of fortuitous coincidences between available laser lines and molecular absorption features. An approach toward tuning the two into resonance with each other was made by Kaldor et al.,[33] who incorporated a sample of air contaminated with NO into a cell placed inside a magnetic-field region. By Zeeman-shifting the NO absorption line into coincidence with the P_{9-8} (13) line of the CO laser, they were able to achieve a sensitivity of 3 ppm. Such a scheme, of course, is not practical for remote sensing in the atmosphere itself. The use of actually tunable infrared lasers, of the sort described in Section II.A, has been reported by Hinkley and Kelley.[34] These authors can achieve a sensitivity of 10 to 20 ppm C_2H_4 in a sample drawn into a 30-cm absorption cell and estimate a lower limit of 1 ppb in a 1-km absorption path. In a very recent report, Alobaidi and Hill[71] have demonstrated the use of the 3.39-μm line of the He-Ne laser to monitor ethanol vapor concentration. Their double-beam, direct-absorption "breath-alyzer" can detect as little as 24 ppm of ethanol in exhaled breath.

The use of a tunable laser may be particularly advantageous in discriminating specific molecular absorption from interfering background attenuation and scattering processes. This can be done by measuring *differential* absorption between adjacent maxima and minima in the absorption spectrum. Such a monitoring system has been proposed for NO_2, using a tunable dye laser operating between 4,300 and 4,500 Å.[35] For a 4-km path, a sensitivity limit of 0.01 ppm (10 ppb) can be attained.

2. Backscatter Techniques

An alternative approach to remote sensing involves the detection of light backscattered from an intense laser pulse propagating through a polluted atmosphere. The processes that are sensitive to the concentration of trace contaminants are either Raman scattering, fluorescence backscattering, or differential absorption of Rayleigh-Mie backscattering. Of these, the Raman method has received the most attention.[36] The advantage that this approach possesses over direct long-path

absorption monitoring is that, by time-gating the returning signal, a range resolution is possible along the path of the beam. Its major disadvantage is its much lower sensitivity, as compared with direct absorption methods.

For example, Kobayasi and Inaba[37] have tested a laser-Raman radar ("Lidar") technique for detection of SO_2 in the atmosphere, using a 10-mW ruby laser source. They found a lower detection limit of approximately 1 ppm; this is comparable with direct-absorption or heterodyne techniques, primarily because there are currently no good laser sources in the SO_2 infrared absorption region. Ahmed[38] has evaluated the sensitivity for NO_2 of differential absorption of elastically backscattered light from a tunable dye laser. He estimated a lower limit of 0.4 ppm at a range of 1 km with a resolution of 100 m, which is still a factor of 50 less sensitive than a comparable reflected-beam absorption experiment.[35] Raman backscattering may prove to be more effective than direct absorption for monitoring species that do not possess sharp absorption features; one example that has been suggested is the remote sensing of the acid content of aqueous aerosols.[39]

Fluorescence backscatter is, in general, even less sensitive than Raman backscatter as a result of extensive fluorescence-quenching at atmospheric pressure. A discussion of laser-induced infrared emission as a remote-sensing technique has appeared in the literature;[40] however, the analysis given for this phenomenon is scientifically incorrect, and the method itself is of no practical value. The primary effect of a high-energy infrared beam propagating through the atmosphere is to heat the column of air along the beam path, a fact that the authors[40] apparently fail to understand. Thus, there can be no specific excitation of any one species contained in the sampled region, making the detection of a single species out of a mixture impossible. A laboratory prototype experiment for detecting ethylene by laser-induced (actually thermal) infrared emission is described in Reference 40; the minimum detectable concentration quoted therein for this method is 1,000 ppm (0.1%), which is a *million times* less sensitive than comparable direct-absorption, spectrophone, or heterodyne-radiometry methods.

C. Instrumental Methods

The application to analytical chemistry with

the greatest potential significance is the use of lasers to replace conventional light sources in commercial spectrophotometric instrumentation. This has already taken place in the area of Raman spectroscopy, and some preliminary development of a laser-atomic absorption/fluorescence spectrometer has been reported, but there seems to have been no real impact in other areas. These various applications will be discussed in more detail in the following section.

1. Laser-Raman Spectroscopy

In Raman spectroscopy, laser sources have completely supplanted the old, cumbersome "Toronto" mercury-arc excitation lamps. Indeed, this field is now thoroughly reviewed and has even matured to the point of being the subject of textbooks.[41] For this reason, we will not go into any further details in this review, except to remark in passing on a few recent developments.

The typical commercial laser-Raman spectrometer employs a c.w., fixed-frequency ion laser as an excitation source. The use of a pulsed dye laser or of a mode-locked argon-ion laser as a source permits the use of time-gated detection electronics to improve signal/noise ratios.[42] Also, increased sensitivity can result from the generation of

stimulated rather than ordinary spontaneous Raman emission. In Coherent Anti-Stokes Raman Spectroscopy (see Figure 4), light at frequencies ω_p and ω_S is applied to a sample, and coherent Raman scattering is observed at $2\omega_p - \omega_S$. The intensity of this stimulated process is about three orders of magnitude greater than ordinary Raman for a given sample concentration. Stimulated Raman scattering can also be generated by combining the beams from a pulsed nitrogen laser and from an N_2-pumped dye laser in the same sample, with the frequency difference between the two corresponding to a Raman-active vibration in the sample.[43] The use of tunable dye lasers to study resonance-Raman emission has been reported in the research literature, but a commercial Raman instrument that incorporates a tunable laser source is not yet available.[44,45]

2. Atomic Absorption/Fluorescence Spectrometry

One major analytical technique that should benefit enormously from the introduction of tunable lasers is atomic absorption/fluorescence spectrometry. The conventional AA-AF spectrometer requires a number of hollow-cathode lamps corresponding to the atomic resonance lines of the different metals to be analyzed. These sources
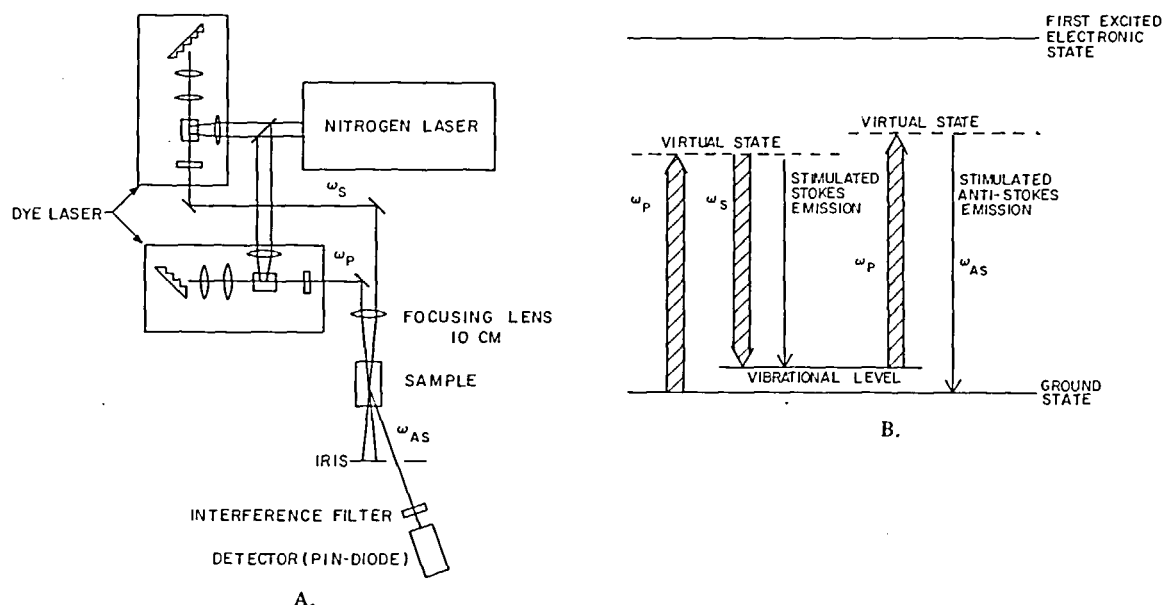

FIGURE 4. Coherent Anti-Stokes Raman Spectroscopy (CARS). A. Schematic diagram of an experimental set-up using a nitrogen laser to pump two dye lasers; the beams are crossed and focused into the sample cell, which is followed by a spatial filter and an interference filter; the output is detected by a photodiode and processed with a dual-channel boxcar integrator. B. Energy-level diagram describing the CARS process. (Reproduced from Molectron Applications Note No. 111. With permission.)

could be replaced by a single tunable dye laser; at most, a series of dyes would be needed to cover the desired wavelength range.

A prototype spectrometer of this type has been developed by Winefordner et al.[46-48] A block diagram of the instrument is shown in Figure 5. A nitrogen-pumped dye laser is used to excite fluorescence in a flame containing metal atoms, and time-gated detection electronics are used. The detection limits for a wide variety of metals are indicated in Table 4 and compare favorably with those obtainable in commercial spectrometers.

Kuhl et al.[49] have used direct absorption measurements from a tunable dye laser source to determine sodium vapor; their reported detection limit of 2 ng/cm³ is also comparable with conventional methods.

Also included in Table 4 are determinations of Cd and Zn atoms by what is stated to be two-photon fluorescence. In these experiments,[47] atomic fluorescence was observed at one half of the indicated wavelength. It is difficult to see just what processes and energy levels could give rise to this observation, since the same upper and lower

states cannot, of course, be connected by both two-photon and one-photon transitions; this is strictly prohibited by parity selection rules. This was not followed up, since it was felt that the sensitivity of these signals was insufficient for analytical applications.

Another approach to detection of low concentrations of absorbing material is to incorporate the absorption cell *into* the cavity of a broad-band dye laser. Since the laser is an amplifying medium, and since the gain is suppressed at wavelengths where absorption is present, the laser output will be reduced or shut off entirely at these wavelengths. This effect was first demonstrated by Peterson et al.;[50] it has been put to use by Holleman and Steinfeld in studies of ICl fluorescence.[51] ICl vapor is unavoidably contaminated with I_2, with which it is in equilibrium, and the fluorescence excitation and emission spectra of the two species overlap badly. By placing an I_2 absorption cell into the dye laser cavity, output at wavelengths capable of exciting I_2 was suppressed, so that the much weaker ICl fluorescence could be easily observed.
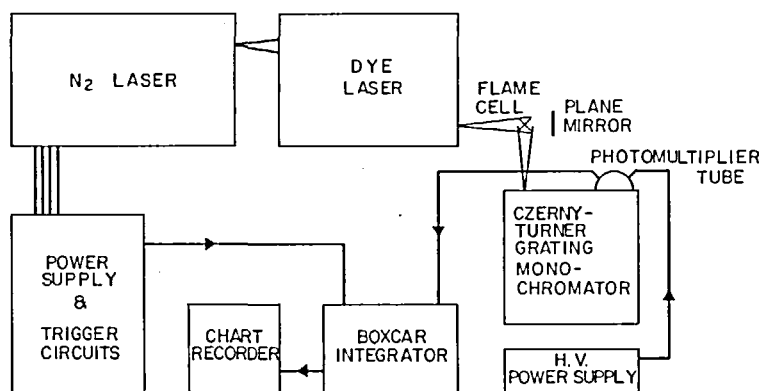

FIGURE 5. Block diagram of experimental system for laser-excited atomic fluorescence flame spectrometry. Instrumental components: Model 1000-N_2 laser with power supply and trigger circuits and Dial-a-Line dye laser, AVCO Everett Research Laboratory, Everett, Mass. 02149; RCA 1P28A photomultiplier tube; Model 4-8400 scanning 0.25-m Czerny-Turner grating monochromator, American Instrument Co., Inc., Silver Spring, Md. 20910; Model 160 Boxcar Integrator, Princeton Applied Research Corp., Princeton, N.J. 08540; Servoriter II Potentiometric Recorder, Texas Instruments, Inc., Houston, Texas 77006; Model 412B high-voltage power supply, John Fluke Manufacturing Co., Inc., Seattle, Wash. 98133; Modified Jarrell-Ash Triflame nebulizer burner and capillary burner mounted on Perkin-Elmer chamber-nebulizer; two-stage regulators on gas cylinders and burner regulator with flow meters for Perkin-Elmer Model 303 atomic absorption flame spectrometer, Perkin-Elmer, Inc., Norwalk, Conn. 06852. (From Fraser, L. M. and Winefordner, J. D., *Anal. Chem.*, 43, 1693, 1971. With permission.)

Several experiments have also been carried out using aqueous solutions of rare-earth ions as intracavity absorbers.[53,54] For Ho^{3+} (aq) and Pr^{3+} (aq), the lower detection limit appears to be about $10^{-4} M$. This corresponds to 20 to 30 $\mu g/ml$, which is a factor of 200 for Ho, and of 3 for Pr, less sensitive than laser-excited atomic fluorescence spectrometry. The lower limit of ca. $0.02 M$ for Eu^{3+} (aq) represents nearly five orders of magnitude less sensitivity than that for fluorescence!

One application in which intracavity absorption may be helpful is in detecting unstable reactive species, such as free radicals, in flames or in flash photolysis. In an experiment of the latter type, the radicals NH_2 and HCO were clearly observed following the photolysis of NH_3 and H_2CO, respectively.[55] Absolute detection limits are not stated, but the total pressure of the parent compounds was less than 1 torr in each case. Thus, the intracavity absorption technique appears to be at least an order of magnitude more sensitive than direct-absorption photoflash spectroscopy.

3. Fluorescence Assay Techniques

Laser-excited fluorescence with tunable sources has come to be an extremely important technique in such research areas as spectroscopy, reaction kinetics, molecular-beam scattering, and so on.[56] By eliminating the analyzing monochromator, and by viewing the fluorescence either directly with a photomultiplier or, at most, through a filter to reject scattered exciting light, a density of absorbing/fluorescing species as low as 5×10^4 cm^{-3} can be detected. Formally, this would correspond to a concentration of 2×10^{-9} ppm, referred to a standard atmosphere. In practice, samples must generally be run at reduced pressure, since quenching of the excited molecules may take place at nearly gas-kinetic collision rates. Nonetheless, laser-excited fluorescence is probably still the most sensitive spectroscopic technique currently available.

Several analytical applications of this technique have recently appeared in the literature. Tucker et al.[57] have monitored atmospheric NO_2 concentrations by excitation with the 4,880-Å line of an argon-ion laser and detection of the long-wavelength fluorescence. The gas samples are drawn into the apparatus at a fixed monitoring point, and a detection limit of 3 ppb at this sample point can be obtained. Ambient NO can also be determined, by preoxidation to NO_2. The presence of 50 ppb (0.05 ppm) of formaldehyde in air at atmospheric pressure can be detected by excit-

ing with a frequency-doubled, flash-pumped dye laser in the 3,200- to 3,450-Å range.[58] There is also the possibility of measuring unstable free radicals; the fluorescence of CH in an oxyacetylene flame, excited by a dye laser at 4,315 Å, has been reported,[59] but no quantitative sensitivity is stated in this instance. A frequency-doubled dye laser operating at 2,822 Å has been used to detect OH radicals in a flowing discharge.[60] A concentration of $[OH] = 10^{12}$ cm^{-3} could be easily detected, and the authors estimate that the ultimately attainable sensitivity should be on the order of 10^7 cm^{-3}, which corresponds to 0.3 ppb at a reduced pressure of 1 torr. Metastable $C_2(a^3\pi_u)$ radicals have been observed in flames by exciting their fluorescence with a dye laser between 5,097 and 5,165 Å; however, no absolute concentrations were established in this case either.[61]

Another area of potential application of lasers is in the fluorescence assay technique extensively used in conjunction with microscopy, chromatography, and the like. A commercial system based on a He-Cd laser (operating at 4,416 or 3,250 Å) has been used in the fluorescence microscopy of very small areas of biological materials.[62] Berman and Zare[63] have demonstrated a laser system for fluorescence reading of thin-layer chromatography plates, which can detect samples of aflatoxins as small as 0.2 ng. Measures et al.[64] have investigated the UV-visible fluorescence characteristics of oil samples. Petroleum and fish oil samples from different locations possess remarkably distinct fluorescence signatures, as Figure 6 shows. Both of the latter investigations used a fixed-frequency ($\lambda = 3,371$ Å) nitrogen laser as the excitation source; however, a tunable dye laser would provide an extra dimension of discrimination between different samples that differ in their UV absorption maxima. Further improvements in tunable UV sources will be required to take advantage of this possibility.

4. Optoacoustic Spectroscopy

An alternative detection method to either absorption or emission is the optoacoustic method. Here, a chopped or pulsed laser beam is absorbed by the species to be detected. The energy thus deposited heats up the gas along the path of the laser beam; the periodic heating produces an adiabatic expansion of the gas, which is in turn detected as a pressure wave by a sensitive microphone. This is really nothing more than the old "spectrophone," but rendered practical by the

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Turnable Lasers and Their Application
in Analytical Chemistry

Jeffery I. Steinfeld

Due to a printer's error, pages 236 and 237 are transposed. In addition, the reference and source line appearing at the end of Table 4 on page 237 bear no relation to that table. The reference appears with Table 1 on page 230 and the source line appears with Table 2 on page 232.

			Reference
			47
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.. ..	403.0	0.1	47
Mo	390.3	0.2	47
Na (absorption)	588.9	0.002	.49
Nd	463.4	2	48
Ni	361.0	0.05	47
Pr	495.1	10	48
Sm	375.6	0.6	48
Sr	460.7	0.01	47
Tb	432.7	1.5	48
Ti	399.8	0.1	47
Tl	377.6	0.02	47
Tm	371.8	0.1	48
Yb	398.8	0.01	48
Zn (2-photon?)	427.6	~10	47

The major problem in this type of experiment is that the laser, while indeed an amplifier of very weak intracavity absorption, is by no means necessarily a *linear* amplifier. The relationship between laser output and single-pass small-signal attenuation depends on a large number of factors, such as the gain of the laser medium, mirror reflectivities, cavity length, and so on. Furthermore, the substance placed in the cavity may act as a saturable absorber at sufficiently high power densities, especially if it is in the form of a low-pressure gas. For these reasons, standardiza-tion of intracavity absorption is rather difficult.

There have been several attempts to use intra-cavity absorption for analytical purposes. Quench-ing of a rhodamine-6G laser by NO_2 and Na has been observed.[52] Quantitative estimates of detec-tion limits for NO_2 are not given, but they appear to be appreciably worse than in long-path direct absorption, described previously, or in laser-excited fluorescence detection, described in the following section. A few ppm of Na can be detected, which compares unfavorably to the 0.002 ppm attainable in direct absorption.[49]
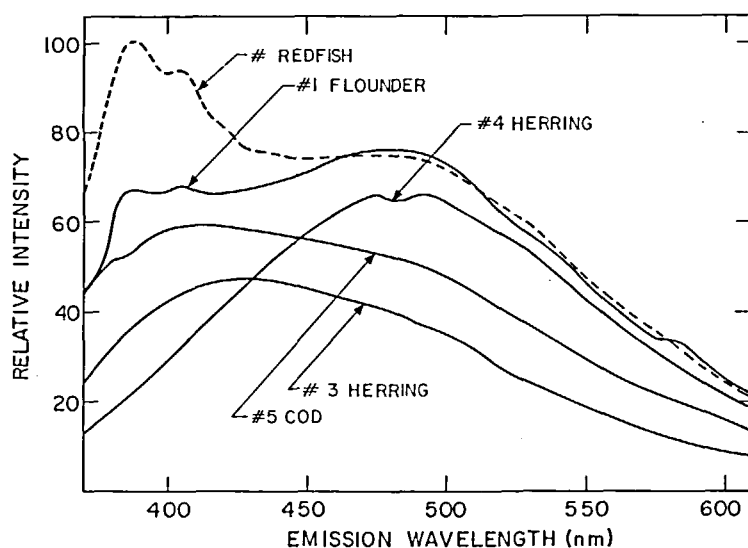
FIGURE 6. Fluorescence spectra of fish oils, excited at 3,371 Å. (From Measures, R. M., Houston, W. R., and Stephenson, D. G., *Opt. Eng.*, 13, 494, 1974. With permission.)

availability of high-power, well-collimated light beams from the laser. In this technique, the sample needs to be at atmospheric rather than at reduced pressure, to ensure that all the energy deposited in internal modes of the molecule is converted to translational energy on a time scale that is short compared to the modulation period. More details of the technique can be found in several reviews.[65,66]

An early application of this technique was in the detection of atmospheric NO.[67] A tunable spin-flip Raman laser was used to pump the NO, and a detection limit of 10 ppb could be achieved. Subsequent improvements, using a series of gas-laser lines, have lowered this limit to the order of 1 ppb for a variety of gases.[30] The use of a tunable dye laser source in a spectrophone apparatus was demonstrated by the Perkin-Elmer Corporation.[68] Appreciable acoustic signals could be obtained from 80 ppm of I_2 vapor in nitrogen, corresponding to a peak optical absorption coefficient of only 3×10^{-5} cm^{-1}. However, most of the emphasis in optoacoustic development to date has been on infrared rather than on visible pumping.

5. Optical Rotatory Dispersion and Circular Dichroism

An additional area of instrumentation in which tunable lasers might be employed to advantage is polarization measurements. The practice of the past 100 years in organic chemistry probably dictates that ordinary polarimetry will continue to be done at the sodium D lines. However, tunable lasers provide a convenient monochromatic, 100% plane-polarized light source for wavelength-dependent measurements, such as ORD, CD, and MCD. To the author's knowledge, no commercial instrument of this type incorporating a laser is now available. Perhaps the further development of tunable UV sources will make this possibility more attractive.

D. Miscellaneous Applications

Freeman et al.[69] have described the use of the 3.39-μm line of the He-Ne laser to monitor concentrations, by absorption, in the effluent of a chromatography column. The particular system investigated was tripalmitin in trichloroethylene. This would seem to be a potentially useful technique, particularly if tunable infrared and/or ultraviolet lasers are used to monitor specific components. Such a detector unit could be incorporated into an automatic fraction collector system; the laser could be used either to monitor the concentrations of eluents in real time, or simply as part of a photoelectric drop-counting system. By contrast, the use of the 6,328-Å line of a fixed-frequency He-Ne Laser as a "colorimeter"[70] would seem to be of little practical utility.
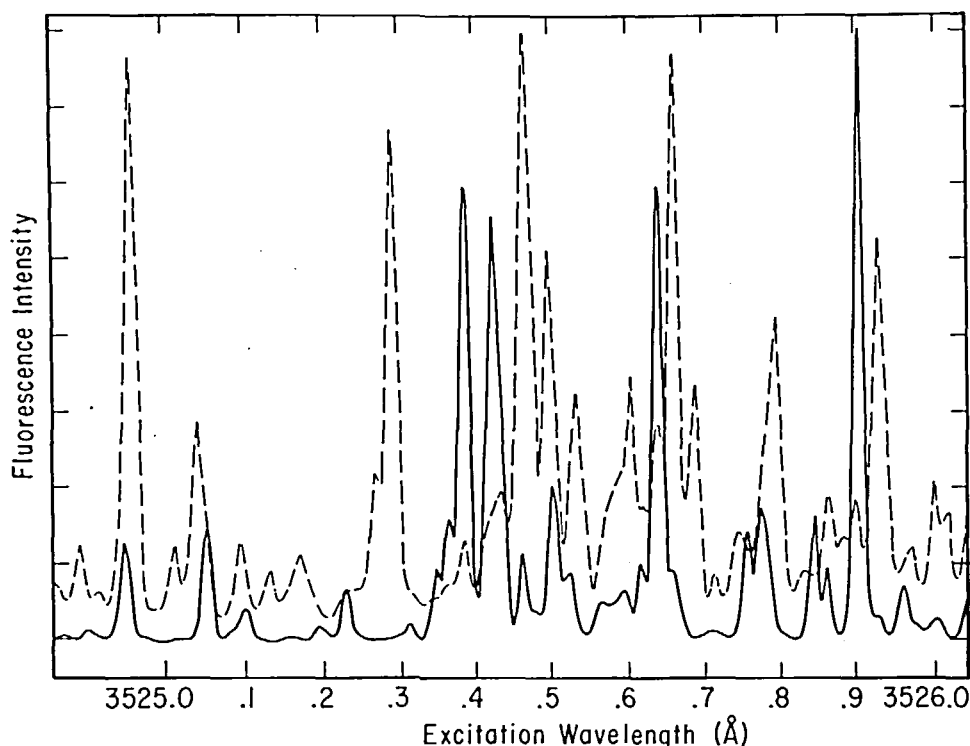
FIGURE 7.   A portion of the high-resolution spectrum of formaldehyde, showing isotopic splittings between $H_2^{12}CO$ (solid line) and $H_2^{13}CO$ (broken line). The spectra were recorded by scanning the ouptut of a tunable ultraviolet laser across the absorption region and recording the formaldehyde fluorescence. The sharp lines at 3,525.29 A and at 3,525.68 A can be used to monitor $H_2^{13}CO$ with minimal interference from the ^{12}C-containing species. (Haas, Y. and Moore, C. B., unpublished results. With permission.)

Another potential application of tunable lasers might be in the determination of the isotopic composition of various materials. This is now conventionally done with expensive special-purpose isotope-ratio mass spectrometers. Equivalent information could be obtained with simple optical absorption measurements on selected isotope-shifted fine-structure lines. In the near-ultraviolet spectrum of formaldehyde, for example (shown in Figure 7), the carbon-12 and carbon-13 lines are easily distinguished from each other, and this region can be probed with a frequency-doubled tunable dye laser.

IV. CONCLUSIONS

The impact that lasers have had on spectroscopy is just starting to be felt in analytical procedures. Major new developments in Raman techniques and remote-sensing ha
place, but not too many other areas have been exploited. The application of lasers to spectroscopic methods of analysis would seem to be a rewarding field, both for research by analytical chemists and for investment by instrument manu-facturers.

ACKNOWLEDGMENTS

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