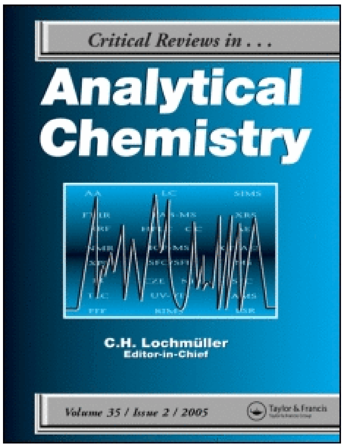

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N. Omenetto; J. D. Winefordner; J. I. Steinfeld

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LASERS IN ANALYTICAL SPECTROSCOPY*

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I. INTRODUCTION

The authors of this review will attempt to present the major advances (up to April 1980) in laser spectrometry, particularly those since the excellent review of Steinfeld[1] in 1975. However, in order to have a consistent treatment, some of the significant articles published prior to 1975 will also be referenced; no attempt will be made to be exhaustive. In addition, we apologize because some of the significant papers, due to oversight, will undoubtedly be omitted. The authors, however, do not intend this review to be a tutorial in laser principles or operation or even on spectroscopic principles or instrumentation, but rather a review of the analytical uses of lasers, including some of the critical aspects of instrumentation and analytical figures of merit.

Although no attempt will be made to discuss in detail the principles of the techniques, the authors felt it would be valuable to include a figure giving the types of transitions involved in most of the laser spectrometric methods to be discussed (Figure 1). In addition, since tunable lasers are used for most of the studies to be reviewed, the figures of merit for several commercial tunable dye lasers, as well as several fixed frequency line lasers, are given in Table 1.

Omenetto and Winefordner[2] have given an extensive treatment of the principles,

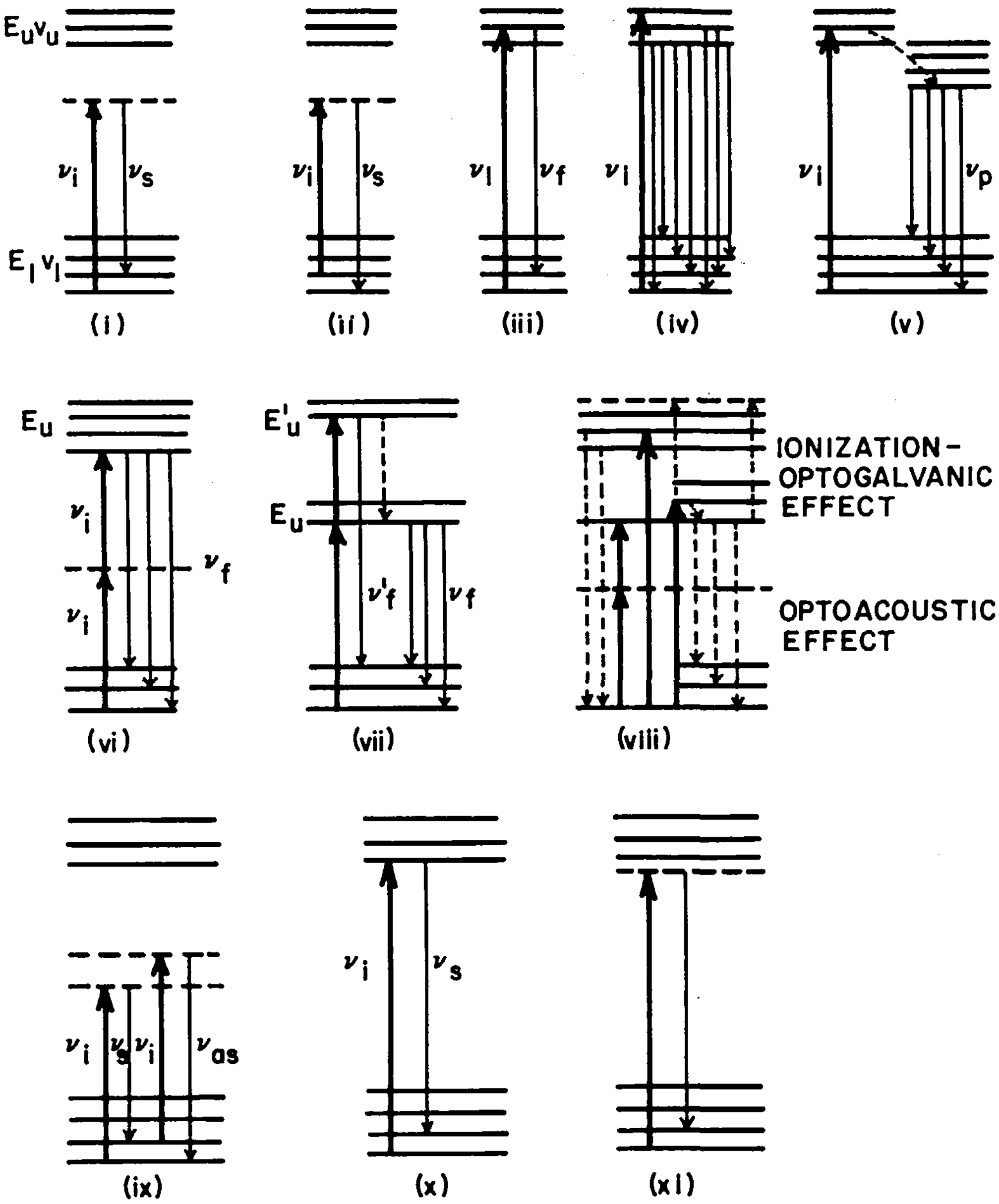

FIGURE 1. Schematic representation of molecular transitions in optical spectrometry. (i) Stokes spontaneous Raman; (ii) anti-Stokes spontaneous Raman; (iii) resonance and Stokes narrow band fluorescence; (iv) broad band fluorescence; (v) broad band phosphorescence; (vi) 2-photon absorption (virtual level) fluorescence; (vii) multiple photon absorption with two lasers (real levels) fluorescence; (viii) optogalvanic and optoacoustic effects; (ix) anti-Stokes coherent Raman scattering; (x) resonance Raman; (xi) near-resonance Raman.

instrumentation, and uses in both combustion diagnostics and analysis of lasers in atomic (and molecular) spectrometry. It is clearly shown that the fluorescence signal depends linearly upon the total concentration of species (as long as the absorbance of absorbers is low) and is independent of quenchers and source irradiance as long as near saturation conditions are approached. Under such conditions, the linearity of the

Table 1
CHARACTERISTICS OF TYPICAL DYE LASERS

Type	Wavelength range (nm)[a]	Power (W)		Resolution (nm)		Pulse width (ps)	Pulse repetition rate (pps)
		Peak	Average	No etalons	With etalons		
Continuous wave dye	≃400—950	—	≃0.02—3	≃0.1—1	0.01—0.001	CW	CW
Synchronously pumped mode-locked dye	≃400—700	≃100—2000	≃0.08—0.1	≃0.1—1	≃0.01—0.001	≃0.5—10	≃100 MHz
Synchronously pumped mode-locked cavity-dumped dye	≃400—700	1—5 kW	≃0.03—0.1	≃0.01—1	0.01—0.001	≃1—20	≳1 pps—10 MHz
Ring dye	≃400—800	—	≳1—3	≃0.1—1	0.01—0.001	CW	CW
N_2-laser-dye	≃210—1000	≃1—300 kW	≃0.01—0.1	≃0.01	≳0.001	≃3000—8000	1—1000
Nd-laser-dye	≃250—1000	≃10 MW	≃0.5	≃0.01	≃0.002	≃10000	≃10
Excimer laser-dye	≃210—1000	≃1—5 MW	≃0.1—0.5	≃0.01	≳0.001	≃10000	≃1—1000
Flashlamp dye	≃260—365; 420—1000	≃10 kW—5 MW	≃0.3—10	≃0.03—5	≃0.1—0.001	≃10^6	≃0.1—30

[a] The range 210 to 360 nm must be obtained by frequency doubling.

analytical calibration curve is increased to even higher concentrations of analyte. It is also shown that the sensitivity of measurement and the detection limits can change considerably if the dye laser beam is expanded in size so as to excite more analyte species, but with the concomitant loss in the near saturation advantages. Finally, under saturation conditions and small laser sizes, the temperatures, concentrations of species, and gas and particle velocities for flames and other environments can be probed both spatially and temporally.

Several other reviews of lasers in chemistry and spectroscopy are available. Among these the reader is referred to the monographs by Omenetto,[3] Hieftje,[4] West,[5] and the article by Robinson.[6]

II. ATOMIC SPECTROMETRY

A. General Comments

Laser excitation of atoms can be probed in four fundamental ways: fluorescence, absorption (intracavity or extracavity), optogalvanic effect, and optoacoustic effect. These methods will be briefly discussed here, with particular emphasis on the analysis of atoms in gases. In Figure 2, the basic instrumental system for laser excited fluorescence and the optogalvanic and optoacoustic effects are given. The principle of operation of these two last techniques will be described in Section VI.

B. Fluorescence

Atomic fluorescence is the most common detection mode in laser excitation of atoms. Although the modulated CW dye laser has been used for a few studies, most of the work has been done with pulsed, nitrogen-laser pumped dye lasers because of their combined advantages of much greater wavelength range, less dye required for operation, and very high peak power.

The N_2-pumped dye lasers and flashlamp pumped dye lasers have been used with flame atomizers,[7-28] furnace atomizers, and with an inductively coupled argon plasma.[36] The CW Ar^+-pumped dye laser has been used with both flame atomizers[17,19,25,26] and with an inductively coupled plasma.[37] Detection limits in the sub ppb (ng/g) range with flame atomizers and in the sub pg range with furnace atomizers have been obtained by laser excited fluorescence spectrometry (Tables 2 and 3). The experimental detection limits are impressive but still do not improve much upon the concentration values obtained by atomic emission inductively coupled plasma spectrometry or by atomic absorption flame spectrometry, or much upon the absolute values obtained by atomic absorption furnace spectrometry. Considerable improvements ($10x - 10^3x$) of the detection limits in laser excited atomic fluorescence spectrometry seem feasible if the calculations based upon signal-to-noise ratios are meaningful (see Section VII). However, perhaps the most important figure of merit in laser excited atomic fluorescence spectrometry is the *selectivity*. By proper choice of laser excitation wavelength and fluorescence wavelength for observation, virtually all spectral interferences can be avoided. In fact, selective excitation can be made even more powerful by use of narrowing techniques to reduce the dye laser bandwidth from ~0.1 nm to ~0.001 nm. In addition, by proper selection of excitation and fluorescence wavelengths, Mie (and Rayleigh, too) scatter can be eliminated. By wavelength modulation of the dye laser wavelength, background (e.g., emission in flames) noise can also be minimized. In conclusion, it should be possible for most atoms to avoid any scatter signal and noise, to improve the detection limits, and to minimize or even eliminate all spectral interferences by proper choices of excitation and emission wavelength.

Measures and Kwong[38,39] have described a trace element analyzer based on laser

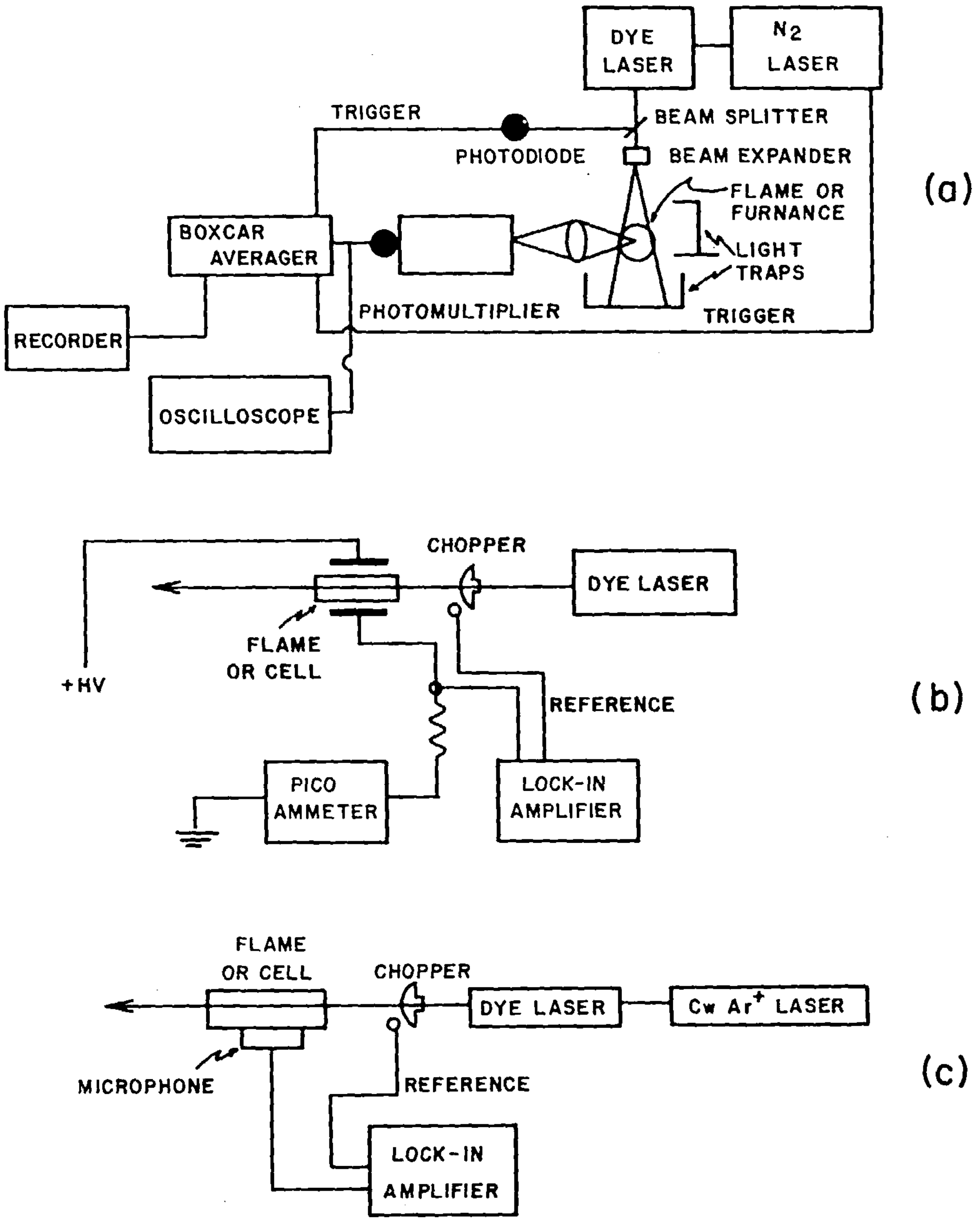

FIGURE 2. Instrumental systems used in (a) fluorescence; (b) Optogalvanic; (c) optoacoustic spectrometry.

ablation and selectivity excited radiation (TABLASER) as a new and reliable microultratrace technique for quantitative *in situ* element analysis. Measurements of trace concentrations of Cr in NBS standard reference steel, Cr-doped flour, and Cr-doped skim milk powder were successfully performed. Currently the detection limits are of the order of 1 ppm in concentration and of the order of subpicograms in absolute amount. In this microprobe technique, a dense high temperature plasma is created by pulsed laser ablation of a solid target, and the resulting hot plume expands into a low vacuum region. After an appropriate delay time, the outward streaming vapor is excited

Table 2
DETECTION LIMITS (AQUEOUS SOLUTION) OBTAINED BY LASER EXCITED ATOMIC FLUORESCENCE SPECTROMETRY AND BY SEVERAL OTHER METHODS

	Detection limit (ng/mℓ)						
Element	Line source[a]	Continuum source[b]	Laser[c]	AAS[d]	AEICP[e]	Opto-galvanic laser[f,g]	ICP-laser
Ag	0.1	1	4	2	0.2(4)	1	—
Al	100	200	0.6	20	0.4	—	—
As	100	—	—	400	2	—	—
Au	1,000	150	—	200	—	—	—
Ba	—	—	8	20	0.01(0.2)	0.2	2
Be	10	15	—	2	—(0.3)	—	—
Bi	10	—	3	30	—(50)	2	—
Ca	20	—	0.08	2	0.0001(4)	0.1	—
Cd	0.001	6	8	1.5	0.07**(1)	—	—
Ce	—	—	500*	—	0.4(20)	—	—
Co	5	15	200*	15	0.1**(2)	—	—
Cr	50	1.5	1	3	0.2(4)	2	—
Cu	1	1.5	1	2	0.04**(2)	100	—
Dy	—	—	300*	—	—(2)	—	—
Er	—	—	500*	—	—(—)	—	—
Eu	—	—	20*	—	—(1)	—	—
Fe	8	10	30(0.06)‡	10	0.09(2)	2	50
Ga	10	—	0.9	—	0.6(40)	0.07	—
Gd	—	—	800*	—	0.5(8)	—	—
Ge	15,000	—	—	—	—(50)	—	—
Hf	—	—	—	200	—(—)	—	—
Hg	80	—	—	—	—(50)	—	—
Ho	—	—	100*	—	—(—)	—	—
In	100	25	0.2	—	—(40)	0.008	300
Li	—	—	0.5	1	—(3)	0.001	—
Lu	—	—	3,000*	—	—(—)	—	—
Mg	1	0.1	0.2	0.2	0.003(20)	0.1	—
Mn	6	2	0.4	3	0.02(0.5)	0.3	—
Mo	500	100	12	20	0.4(5)	—	—
Na	100,000	—	<0.1	0.5	0.02(10)	0.05	—
Nb	—	—	1,500*	—	0.2(20)	—	—
Nd	—	—	2,000*	10	—(10)	—	—
Ni	3	25	2(0.5)Δ	—	0.2(6)	7	—
Os	—	—	150,000*	15	—(200)	—	—
Pb	10	50	13	—	1**(20)	0.6	—
Pd	1,000	100	—	—	2(40)	—	—
Pr	—	—	1,000*	—	—(30)	—	—
Pt	50,000	700	—	—	—(30)	—	—
Rh	3,000	—	100*	—	—(30)	—	—
Ru	—	—	500*	—	—(60)	—	—
Sb	—	—	50*	30	—(30)	—	—
Sc	—	—	10*	—	—(1)	—	—
Se	40	—	—	250	1***(20)	—	—
Si	600	—	—	100	—(10)	—	—
Sm	—	—	100*	—	—(10)	—	—
Sn	30	150	—(3)Δ	70	3(6)	3	500
Sr	30	0.9	0.3	1	0.003(0.2)	—	—
Tb	—	—	500*	—	—(—)	—	—
Te	5	—	—	70	—(20)	—	—

Table 2 (continued)
DETECTION LIMITS (AQUEOUS SOLUTION) OBTAINED BY LASER EXCITED ATOMIC FLUORESCENCE SPECTROMETRY AND BY SEVERAL OTHER METHODS

	Detection limit (ng/mℓ)						
Element	Line source[a]	Continuum source[b]	Laser[c]	AAS[d]	AEICP[e]	Opto-galvanic laser[f,g]	ICP-laser
Ti	—	200	2	80	0.03(1)	0.2	—
Tl	8	6	4	30	—(75)	0.09	—
Tm	—	—	100*	—	—	—	—
V	70	30	30	50	0.06(2)	—	—
Yb	—	—	10*	—	—	—	—
Zn	0.02	15	—	1	0.1(2)	—	—

[a] The values come from references within Winefordner, J. D., *J. Chem. Ed.*, 55, 72(1978).
[b] The values come from Johnson, D. J., Plankey, F. W., and Winefordner, J. D., *Anal. Chem.*, 46, 1858(1974).
[c] Values from Weeks, S. J., Haraguchi, H., and Winefordner, J. D., *Anal. Chem.*, 50, 360(1978), except those with * which were taken from references listed in Winefordner, *J. Chem. Ed.*, 55, 72(1978). The one with ‡ was taken from Epstein, M. S. et al., *Spectrochim. Acta*, 35B, 233(1980), and that with Δ was taken from Epstein, M. S. et al., *Appl. Spectrosc.*, 34, 372(1980).
[d] All values come from Perkin Elmer atomic absorption commercial literature on the Model 460.
[e] All values from Boumans, P. W. J. M. and de Boer, F. J., *Spectrochim. Acta*, 30B, 309(1975), except for those with ** and those in ( ). All values in ( ) come from commercial literatures from Jarrell-Ash Division, Fisher Scientific Co., Waltham, Mass. for their third generation ICP plasma Atom Comp. All values with ** come from Olson, K. W., Haas, J. W., and Fassel, V. A., *Anal. Chem.*, 49, 632(1977).
[f] Values taken from Turk, G. C. et al., *Anal. Chem.*, 51, 1890(1979).
[g] Values taken from Epstein, M. S. et al., *Anal. Chim. Acta*, 113, 221(1980); the ICP is the atomizer and the laser is the excitation source: laser excited fluorescence is measured.

by an interrogating laser pulse ($\sim$6 ns) to saturate an appropriate transition, and the fluorescence is measured. In this method, Mie scatter from particles is small (due to the delay time); most of the elemental species exist in their ground state due to rapid gaseous kinetic processes; the plasma background emission is small; few chemical compounds form due to the low pressure; and dye laser fluctuations (for the saturation process) cause minimal difficulties.

Meng and Kunze[40] studied the diffusion of impurity atoms in plasmas by laser excited fluorescence. These workers produced a pulse of Al atoms into H_2 gas and a plasma by focusing a TEA CO_2 laser beam onto a solid target. As in the previous work, the atoms produced were interrogated by means of dye lasers tuned to one of the resonance transitions, and the resulting atomic fluorescence was measured. Diffusion of the Al atoms into various environments was studied.

Miron et al.[41] used laser induced fluorescence spectroscopy of atomic uranium produced within a pulsed hollow cathode discharge. The saturation of Na in a H_2-O_2-Ar flame and the distribution of population in the various levels produced by one- and two-photon excitation with a tunable dye laser has been studied by Alkemade and co-workers.[42-44] These studies have considerable potential analytical implication. Blackburn et al.[26] have also investigated the saturation behavior of sodium in hydrogen-based flames, while Omenetto et al.[45] and Lucht and Laurendeau[45a] have investigated both theoretically[45,45a] and experimentally in different flames[45] the ratio of the sodium D-lines under laser excitation.

Table 3
ABSOLUTE DETECTION LIMITS (AQUEOUS) SOLUTIONS BY LASER EXCITED ATOMIC FLUORESCENCE SPECTROMETRY AND BY SEVERAL OTHER METHODS

	Detection limit (pg)			
Element	**Laser AFS**[a–c]	**Conv. AFS**	**AAS**[d]	**AEICP**[e]
Cs	1.5[c]	—	100	—
Fe	0.75[a]	—	3	90
Pb	0.075,[a] 0.01[c]	10	5	1000
Tl	0.03,[b] 0.025[c]	20	3	—

[a] Values taken from Bolshov, M. A., Zybin, A. V., Zybina, L. A., Koloshnikov, V. G., and Majorov, I. A., *Spectrochim. Acta,* 31B, 493(1977).

[b] Values taken from Hohimer, J. P. and Hargis, P. T., *Anal. Chim. Acta,* 97, 43(1978).

[c] Values taken from Hohimer, J. P. and Hargis, P. T., ACS Summer Symp. Anal. Chem., West Lafayette, Ind., June, 1979.

[d] Values taken from Perkin Elmer literature.

[e] Values taken from Fassel, V. A., Special Tech. Publ. Am. Soc. Test. Mater., Philadelphia, 1977.

Although the interesting work by Wright[46–50] does not fit in this section, the present review has no better section for it to appear within. Wright has used selective excitation by a pulsed N_2-pumped dye laser to excite selectively the luminescence of lanthanide type ions as probes for detection and measurement of nonfluorescence ions, e.g., Eu^{3+} acts as a spectroscopic probe for $BaSO_4$ precipitates in order to detect the presence of PO_4^{3-} ions. The Eu^{3+} ions whose crystal field levels are perturbed by nearby PO_4^{3-} ions are excited selectively over other Eu^{3+} ions in the lattice giving a direct measure of PO_4^{3-} concentration. On the other hand, using conventional coprecipitation methods, lanthanide ions can be selectively determined in CaF_2 after proper ignition of the precipitate. Gustafson and Wright[47] were able to detect 25 fg/mℓ of Er by precipitating 0.06 mol CaF_2 from 40 mℓ of solution. The method was shown to be interference-free. A recent review by Wright et al.[49] indicates the power of this approach, namely the low detection limits, the selectivity of measurement, and the long linear dynamic ranges. The method is currently adaptable to 15 elements. The major analytical limitation appears to be the tedious, lengthy sample and standard preparation.

Johnston and Wright[48] have developed an ultratrace method of nonfluorescent rare earth (La, Ce, Gd, Lu, as well as Y and Th) using the technique of selectivity excited probe ion luminescence (SEPIL). An Er^{3+} ion acts as a fluorescence probe in CaF_2 precipitates containing the nonfluorescent ions coprecipitated in the lattice. The Er^{3+} ion in combination with the nonfluorescent species produces a new crystallographic site for selective excitation with a dye laser. The detection limits are of the order of >4 pg and a RSD of ~5% is obtained. SEPIL has also been applied to the trace determination of nine lanthanides without prior separation using coprecipitation on CaF_2 and then 4f-electron solid state luminescence after dye laser excitation.

C. Absorption

Intracavity absorption (atomic and/or molecular) and extracavity absorption atomic spectrometry has not been shown to have much analytical utility because of the lack of sensitivity, the nonlinearity of response, and the greater experimental difficulties of making measurements within the dye laser cavity. The significant papers on intracavity absorption are References 51 to 74. Several conclusions are evident by reviewing these articles: (1) cw dye laser systems are more sensitive than pulsed systems and the pulsed systems with longer pulses are more sensitive than those with shorter pulses; e.g., absorptions of the order of 10^{-5} have been detected; (2) intracavity absorption is more sensitive than extracavity absorption; (3) the sensitivity of intracavity absorption is maximized by matching the cavity length with the sample cell length and by using a broadband cw dye laser with a three-mirror cavity (detection of absorption coefficients as small as 10^{-8} cm^{-1}); (4) intra- or extra-cavity absorption can be applied to atoms in flames or hot gases,[55-60,61] gaseous molecules,[73] and radicals in gases, flames, etc., e.g., I_2, OH, NO, CH, NH_3, CH_4, and to ions and species in the condensed phase; (5) diode arrays[54] can be used as the detection device with a concomitant increase in accuracy of data collection but a decrease in resolution as compared to photographic plates; (6) intracavity absorption has also resulted in detection of weak Raman signals;[61] and (7) isotope analysis via intracavity absorption is a definite possibility.[69,72]

Manabe and Piepmeier[75] have made temporally and spatially resolved atomic absorption measurements using a 1 μs dye laser beam to atomize solid samples and pulsed hollow cathode lamps as AA sources. Quentmeier et al.[76,77] and Kantor et al.[78] have used atomic absorption spectrometry to analyze solid samples following vapor production with a focused pulsed laser (Nd-YAG and Ruby lasers, respectively), i.e., laser microprobe atomic absorption spectrometry. In the former work, the pulsed laser produced plume from solids is measured directly (subnanogram detection limits), while in the second case, the vapor aerosol produced is transported into an air/C_2H_2 flame. Van Deijck et al.[79] have assessed the laser microprobe atomic emission spectrometry (cross-excitation with a spark) for trace element analysis; they have found poor precision and thus indicated that this approach should not be used for quantitative analysis. Ishizuka and Uwamino[80] have used laser vaporization with microwave excitation to determine elements in brass, steel, and aluminium alloys; precisions of 1.2 to 13.8% and detection limits (on the solids) of ppm and pg levels were obtained.

D. Optogalvanic Detection

Laser enhanced ionization of atomic species[81-100] in flames[82-85,89,95-98] and gas discharges[81,86-88,90-96,99,100] (called optogalvanic detection) has been shown by Travis et al.[85,97,98] to be an extremely sensitive and selective method for analysis of atoms and molecules. The principle of operation[85] appears to be laser selective excitation of a ground (or thermally excited) state and then thermal ionization of the resultant excited state. Recently, stepwise excitation by two N_2-pumped dye lasers has also been shown to give considerable sensitivity enhancement as opposed to a single photon excitation (without frequency doubling) dye laser. Nevertheless, up to this time, single photon excitation (one laser) with frequency doubling produces better detection limits in most cases than the use of two dye lasers and stepwise photoexcitation.

Travis et al.[85] have given a theoretical treatment of the signal level. The resulting ionization is detected by the nonselective process of current flow via two polarized electrodes placed near the flames (or discharge). The detection limits (see Table 2) by this approach have been found to be in the sub ppb level for many atoms. Although the technique is extremely sensitive, it is still doubtful whether it will have great analytical use because of the swamping effect of background electrons (ions) in hot flames needed to efficiently atomize complex samples. So far, optogalvanic signals have been obtained for more than 20 elements in flames as well as rare gases in flow discharges.

E. Optoacoustic Detection

Allen et al.[101,103] have used the optoacoustic effect (see Section VI) to obtain pressure pulses from flames following interaction of laser energy with an electronic transition. Optoacoustic detection is a unique means of studying the nonradiative deactivation (quenching) processes in atomic fluorescence spectrometry. By such measurements, it is possible to obtain energy transfer rates, collision half-widths, and quenching rates. Allen et al.[101-103] have studied Na in an air per C_2H_2 flame with a Chromatix® CMX-4 flashlamp pumped dye laser.

The optoacoustic effect has been shown to have potential analytical use by Howard and Greenhalgh,[104] although the sensitivity obtained for sodium was not very good.

III. MOLECULAR ABSORPTION SPECTROMETRY

A. General Comments

Molecular absorption spectrometry with tunable lasers has been used to identify and determine trace species in the gas phase and in the liquid phase. In the gas phase at low pressures, Doppler-free techniques[105-106] and narrow band tunable dye lasers or narrow band fixed frequency lasers have been used to obtain high resolution uv-visible electronic absorption spectra. Resolving powers approaching 10^{12} are possible by Doppler-free methods. These exciting techniques, however, have found little use for quantitative analysis and so will not be discussed further here. High resolution in vibrational-rotational spectra have been obtained with a variety of laser types, including: the semiconductor diode lasers (wavelength range of $\simeq 1$ to 34 μm, capable of $\lesssim 3 \times 10^{-6}$ cm^{-1} resolution); the spin-flip Raman lasers (range of $\simeq 5$ to 6.5 μm and 9 to 14.6 μm with a resolution of $\lesssim 3 \times 10^{-6}$ cm^{-1}); the nonlinear devices, including the parametric oscillator (wavelength range of <1 to 11 μm and a resolution of $\lesssim 3$ to 10^{-2} cm^{-1}), the difference frequency generator (wavelength range of 2 to 6 μm and resolution of $\lesssim 5 \times 10^{-4}$ cm^{-1}), two photon mixing (wavelength range of 9 to 11 μm and a resolution of $\lesssim 3 \times 10^{-5}$ cm^{-1}), and four photon mixing (wavelength range of 2 to 25 μm and a resolution of $\lesssim 2 \times 10^{-1}$ cm^{-1}); and gas lasers, including Zeeman-tuned devices (wavelength range of 3 to 9 μm and a resolution of $\lesssim 3 \times 10^{-3}$ cm^{-1}) and a high pressure CO_2 laser (wavelength range of 9 to 11 μm and a resolution of $\gtrsim 3 \times 10^{-5}$ cm^{-1}).

Moderately high resolution spectroscopy (resolution of $\gtrsim 0.1$ cm^{-1}) is primarily useful for gas phase studies. In the liquid or solid phase, resolution below 1 cm^{-1} is seldom needed or desired, and so conventional dispersive spectrometers are used in the uv-visible-near ir region and in the ir region; in the ir region, Fourier Transform and Hadamard Transform spectrometers also can be used. However, with tunable lasers, the spectrometer acts merely as a tunable filter to isolate the spectral region of interest.

Laser absorption experiments generally involve either *differential* or *derivative* absorption measurements. The basic experimental system for either system is shown in Figure 3. The differential absorption signal of flux $\Delta\phi$ is

$$\Delta\phi = \phi_0 - \phi_1 = \phi_0(1 - e^{-k\ell}) \xrightarrow{k\ell \lesssim 0.05} \phi_0 k\ell \qquad (1)$$

where k is the linear absorption coefficient in cm^{-1}, ℓ is the absorption path length in cm, ϕ_0 is the incident flux, and ϕ_1 is the transmitted flux. Absorptions as small as 10^{-4}, i.e., $\Delta\phi/\phi_0$, can be measured, assuming the noise level is low enough (see Section VII). For a path length of 1 m, it is possible to detect 10^{11} to 10^{12} molecules per cm^3, which correspond to 10 to 100 ppb (ng/g) at atmospheric pressure (10 to 100 ppt (pg/g) can be detected for a 1 km pathlength).

If the laser frequency is modulated around the absorption line or band,[107] then the ac

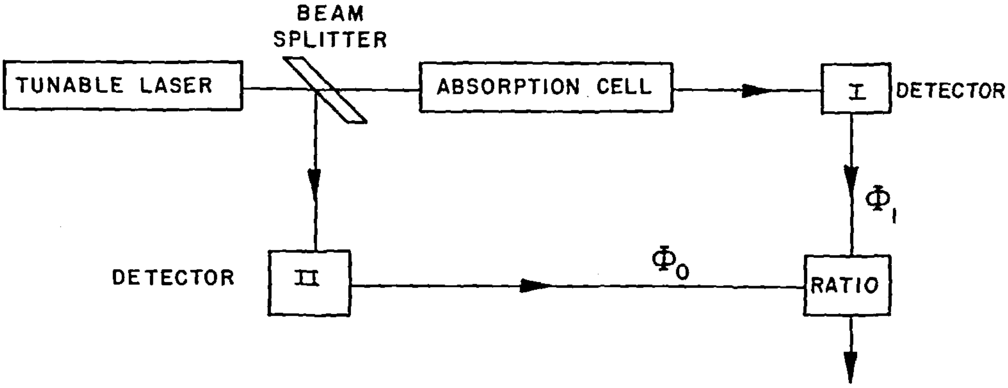

FIGURE 3. Instrumental system used in differential and derivative absorption spectrometry.

signal component can be measured at the modulation frequency; this technique is called *derivative absorption.* If the electronic measurement system is tuned to the modulation frequency, and if the wavelength modulation interval is small compared to the spectral feature of interest, a first derivative spectrum results. If the electronic measurement system is tuned to twice the modulation frequency, and if the wavelength modulation interval is small, then the second derivative of the spectrum results. Using wavelength modulation, absorptions as small as 10^{-8} can be measured because of the minimization of low frequency noise in the light source; in addition, wavelength modulation methods are superb means to isolate spectral features from broad band interferences.

Recently, Harris and Dovichi[108,109] have shown that the *thermal lens effect* can be used for calorimetric trace analysis. The thermal lens effect, generated by the laser beam, produces a loss of radiation energy in the beam center, depending on the laser power. There is no need for a double-beam system since the time dependence of the effect provides a blank measure. With a 4-mW He-Ne laser, a detection limit of 3.3 ng was found for Cu(II) present as an EDTA complex.

B. Doppler-Free Two-Photon Spectrometry

Gelbwachs[110-112] has used a narrowed N_2 dye laser for Doppler free spectroscopy of NO, benzene, naphthalene, etc. Doppler-free two photon spectroscopy involves irradiation of a gas sample with oppositely directed (see Figure 4) optical beams at a frequency corresponding to one half of the molecular (or atomic) transition frequency. Simultaneous absorption of one photon from each of the counter propagating beams results in absorption, free from Doppler broadening.[105,106] The two photon absorption profiles are much narrower and give more intense peaks than Doppler broadened two-photon absorption profiles. Such a measurement approach can be used for monitoring of atomic and molecular gases (including on-site monitoring of stratospheric gases). Detection limits of the order of 10^5 to 10^7 molecules per cm^3 are feasible for molecular species with strong two-photon uv-absorption transition.

Gelbwachs and Wessel[129] have indicated that perhaps the most exciting future use of Doppler-free two-photon absorption lies in the area of large molecule spectroscopy. For example, the major problem with large molecules using conventional absorption spectrometric approaches is spectral congestion, i.e., rotational structure of electronic transitions in gaseous molecules the size of benzene or larger is so complex that Doppler broadening causes near complete overlap of adjacent transitions. Therefore, the typical high resolution absorption spectrum of a complex large molecule is a smooth,

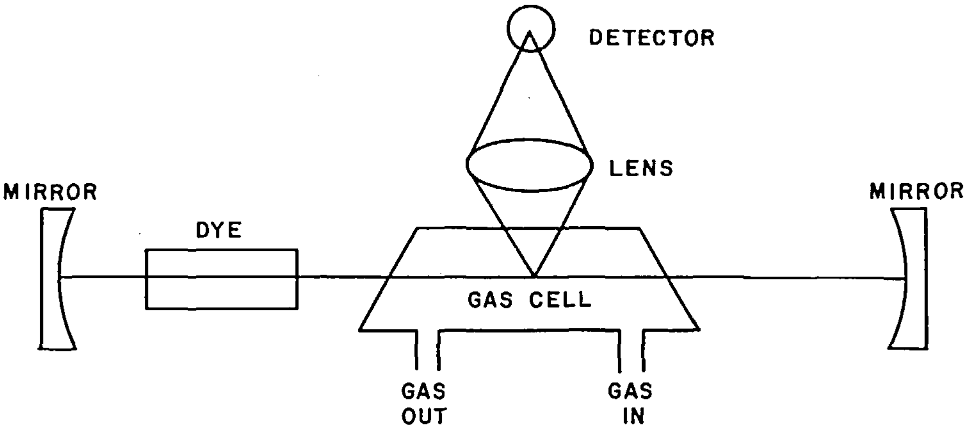

FIGURE 4. Instrumental system used in Doppler-free spectroscopy.

continuous, undifferentiated band that covers the entire region of rotational-vibrational bands contributing to the electronic transition. However, even at room temperature, molecules with $\gtrsim$ 25 atoms are unlikely to yield resolvable spectra even when Doppler-free spectroscopy is used.

Two-photon absorption is critically dependent upon laser intensity, bandwidth, and coherence. Therefore, for most two-photon studies, gas lasers providing a single TEM_{00} mode operation are needed. Pulsed studies are highly dependent upon pulse shape and are not useable unless pulses are of known and reproducible spectral, temporal, and spatial form.

The uv region is optimal for detection of trace gases. In the uv region, single photon absorption transition probabilities are high. However, single photon excitation in the uv is difficult because of the lack of narrow band, tunable lasers (especially CW). However, in the visible region, with Doppler-free two-photon absorption, molecular absorption bands are sharp (because of the minimization of the Doppler broadening) and tunable narrow band CW dye lasers are readily available.

C. Pollution Analysis

The majority of articles involving laser molecular absorption have involved gas analysis of pollutants. Patel[133] and Measures[114] have reviewed various absorption (as well as scatter and fluorescence) methods for pollution measurements.

UV absorption of pollutants can be measured using the so-called DIAL method (uv differential absorption LIDAR method, see Figure 5). In this method, a frequency doubled-pulsed dye laser with receiver telescope is used; the dye laser is tuned to two wavelengths, corresponding to a maximum and a minimum in the absorption spectrum. As the pulsed laser radiation travels through the atmosphere, Rayleigh and Mie backscatter is measured as a function of the range through the use of standard LIDAR range gating techniques. Differences in the backscatter radiation from the two transmitted wavelengths can be related to the column content of the absorbing gas between the transmitter and the scattering column. The distribution of the absorbing gas as a function of range can be obtained from the difference between column content measurements made at different ranges.

The uv DIAL method has been used to detect 20 ppb of SO_2 at range of up to ~2 km by Hoell et al.[115] Kuhl and Spitschan[116] used a similar method to determine SO_2 (detection limit <1 ppm at 1 km) in a smokestack plume. O'Shea and Dodge[117] have used an Ar^+

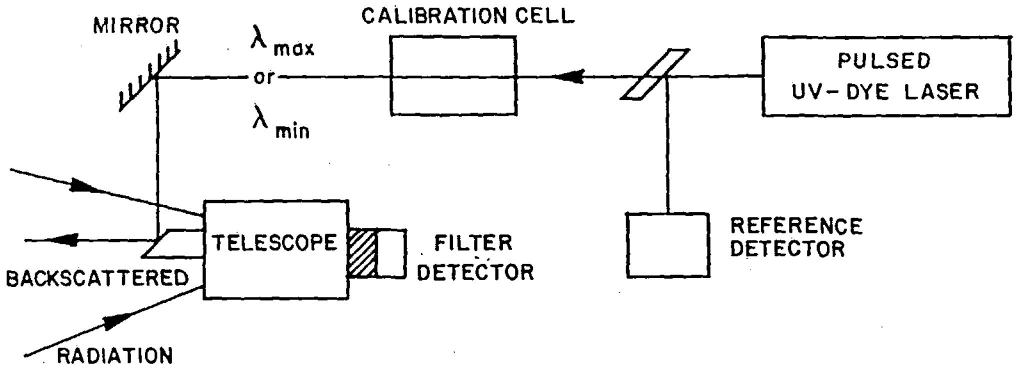

FIGURE 5. Instrumental system used in UV-differential absorption laser spectrometric methods (DIAL).

laser to determine NO_2; these authors were attempting to devise a method for measuring NO_2 in the troposphere. No results were given in the latter study; however, the latter authors did monitor NO_2 in the 0.03 to 0.25 ppm level in several urban environments. Murray et al.[118] have used a DF laser and the DIAL method to detect HCl, CH_4, N_2O in a remote sample chamber. These authors were able to detect HCl, CH_4, and N_2O at 0.05, 6.0, and 0.24 ppm/km. Rothe et al.[119,120] have measured NO_2 over the city of Cologne using DIAL and have obtained a detection limit of 0.05 ppm/km. Byer et al.[121,122] have used a tunable optical parameter oscillator to measure CO and SO_2 in an absorption cell located about 100 m away; the detection limit for SO_2 was <1 ppm/km.

Megie and Menzies[123] have shown the complementary character of uv and ir DIAL for global measurements of atmospheric species. Generally, it was shown that ir systems have advantages in lower atmospheric measurements and uv systems are superior for middle and upper atmospheric measurements. A lidar system with tunable dye lasers and a 25 cm Newtonian telescope has been constructed and used in atmospheric pollution monitoring (SO_2 and NO_2) by Fredriksson et al.[124]

Halpern et al.[125] have described a unique method of remote atmospheric sensing based upon multiphoton sequential photodissociation. In this method, an ArF excimer laser (193 nm) has been used to determine NH_3. Tonnissen et al.[126] have measured HF in the exhaust of an aluminum plant by resonance absorption of a cw chemical HF laser; the simultaneous absorption of H_2O and CO_2 at the HF laser line was accounted for.

The monitoring of pollutants over long path lengths has been the most useful means of obtaining the average concentration of pollutants over that path length. Long path measurements can either be made in the *single-ended* or *double-ended* modes. In the double-ended mode, a tunable laser is at one end and a detector at the other end of the long path, whereas in the single-ended mode, a retro-reflector is used to reflect the source radiation back to the detector which is positioned near the source. A third approach is based upon heterodyning, where a tunable source, such as a diode laser, is used as a local oscillator and beat against emission radiation from the pollutant or absorbed radiation from a distant source like the sun.

Early in 1971, Hinkley and Kelley[127] reviewed the use of diode lasers, e.g., $Pb_{1-x}Sn_xTe$ for ir absorption of pollutants. They have discussed the measurement of the concentration of NH_3, of SF_6, and of C_2H_4 from automobile exhaust, all at low pressure to minimize collisional broadening. Detection limits of <1 ppm/m were obtained. They also discuss long path atmospheric measurements with diode lasers, especially for the detection of SO_2. Diode lasers have also been used for remote emission detection of pollutants in smoke stacks, e.g., SO_2 can be detected at concentrations exceeding 10 ppm.

Atmospheric turbulence can be minimized by alternately tuning the laser source between the peak emission wavelength of the pollutant and a wavelength of negligible emission in a time short ($\lesssim$1 ms) compared to the turbulence, and then summing the excess pollutant signal for a large number of measurement intervals. Two local oscillators could also be used, one operating at the emission peak and one off the peak. For a recent survey of diode laser literature, the reader is referred to the review of Eng et al.[127a]

Hinkley et al.[128,129] and Nill[130–132] discussed the advantages and characteristics of tunable diode lasers for structural and quantitative analysis. Hinkley et al.[129] have used a tunable diode laser for long path monitoring of NH_3, ethylene, vinyl chloride, Freon, and O_3. The predicted detection limits for 1 km absorption paths are in the low ppb/km range. These five molecular species could be determined with a single diode laser system. Wahlen et al.[131] have measured the absorption coefficient for $^{14}CO_2$ and have discussed the interesting possibility of determining ^{14}C in organic compounds by combustion to CO_2. Presumably in the latter case, the only possible spectral interferences would be from N_2O and $^{13}CO_2$. However, by measuring the P branch of $^{14}CO_2$, no interference from $^{13}CO_2$ would result, and in addition, by measuring the R branch of $^{14}CO_2$ which extends into the P branch of $^{13}CO_2$, both $^{14}CO_2$ and $^{13}CO_2$ could be measured. Nill[132] has predicted detection limits of the order of sub-ppb/km for a number of small molecules, including CO, SO_2, NO, O_3, and C_2H_4.

Reid et al.[133] have described a diode laser ($Pb_{1-x}Sn_xSe$) spectrometer capable of detecting absorption coefficients as small as 10^{-7} m^{-1}. The sensitivity of the system for pollutant gases is in the ppb range for SO_2, O_3, N_2O, H_2O, NH_3, and PAN, but could be improved ~100 times by using additional diodes.

El-Sherbing et al.[134] have accurately measured 100 lines in the ν_3 band of ozone with a semiconductor diode laser and have monitored ozone in the presence of other molecular species (detection limit of ~0.5 ppb). Eng et al.[135] have improved the detection sensitivity of long path atmospheric monitoring with tunable diode lasers; these workers used the results of noise studies to obtain an optimum modulation frequency. Chaney et al.[136] have used a diode laser for long path absorption of CO; the diode laser in frequency stabilized by automatically correcting the laser current and is limited to a single wavelength output by a tunable etalon. Hanson[137] has shown the feasibility of a tunable diode laser to study CO absorption in a sooty C_2H_2 per air flame.

Granatstein et al.[138] described a remote sensing method based upon backscatter of a He-Ne laser from particles in smokestack plumes. By use of two laser wavelength, one for resonant absorption and one for backscatter, the concentration of the pollutant can be determined. Kusnowo et al.[139] have used a He-Ne laser and a multipath cell to measure the saturated absorption signal of CH_4 at 3.39 μm. Koike and Gardner[140] have measured high temperature (1000 to 3000 K) absorptivities of propylene, acetylene, and ethylene with a He-Ne laser at 3.39 μm.

In 1971, Menzies[141] showed that the spectral coincidence of CO laser emission lines with absorption lines of NO, NO_2, SO_2, and CO allows measurement of these species based upon resonant absorption, thermal emission, or fluorescence. Wide band heterodyne receivers and thermal emission appeared to offer the greatest sensitivity. Hillman et al.[142] have coupled a CO_2-laser with a tunable diode laser for heterodyne calibration of molecular spectra; stability of ±2 MHz was obtained.

Freund et al.[143,144] have used narrow band gas lasers (CO or CO_2) and the Stark effect to quantitatively measure vinyl chloride in air and NO_2 in N_2 (both in the ppm range). The authors indicated that absorption by molecules having no dipole moment did not interfere because their absorption was not modulated. Of 14 chemicals possibly present in industrial atmospheres, including Freon 11, Freon 12, Freon 113, acetone, acrylonitrile, chloroform, methanol, methyl chloride, methyl fluoride, toluene, tetrohydrofuran, trichloroethylene, vinyl acetate, and vinylidene chloride, no spectral interference should occur (except for acrylonitrile) for vinyl chloride measurements. In addition, several of these species could be quantitatively measured by the Stark effect, laser absorption experiment. Sweger and Travis[145] have applied infrared lasers (CO and CO_2) to the selective detection of trace organic gases (vinyl chloride, vinylidene chloride, acrylonitrile, and methanol) of industrial importance. For molecules with a permanent dipole moment, the molecular energy levels can be tuned so that the absorption lines coincide with one of the laser lines; detection limits in the ppm range were obtained in all cases, together with linearity of calibration curves over several orders of magnitude.

Menzies and Shumate[146] have measured the ambient air pollutants O_3, NO, and C_2H_4 in the Pasadena area using a bistatic IR absorption laser system. Both direct detection of laser radiation (CO and CO_2 lasers) with a retroreflector and heterodyne detection were used. In the 5 to 12 μm wavelength region, heterodyne detection of scattered ir radiation was 10^4 to 10^5 times more sensitive than direct detection of ir absorption. The detection limit for O_3 over a 1 km path was 2 ppb.

Kanstad et al.[147] have used a dual line CO_2 laser for atmospheric spectroscopy and laser monitoring of pollutants, including H_2O, O_3, NH_3, SO_2, C_2H_4, vinyl chloride, Freon 11, and Freon 12. Ethylene can be detected by differential absorption spectroscopy at 0.5 and 2 ppb across a 1200 m path in a calm and in a turbulent atmosphere, respectively.

Golden and Yeung[148] have discussed long path absorption spectroscopy with narrow line ir lasers and have described the means of selecting resonant frequencies for gas analysis, particularly for the pollutants O_3, N_2O, CO, and CH_4 in the presence of nonpollutants H_2O and CO_2. Green and Steinfeld[148a] have described a simple, long-path laser absorption method which is capable of resolving complex mixtures of closely related trace contaminants at ppm levels. A frequency-stabilized CO_2 laser was used to determine the absorption coefficients of several gases representative of the types of contaminants expected to build up in recycled atmospheres.[148b,148c]

D. Other Studies

Hoge and Kincaid,[149] using a coaxial dual-channel laser, measured the absorption coefficients of highly absorbing liquids in the uv. The uv laser power in the transmission channel, coupled with the wide variability of differential path lengths measurable with a reflective channel, gave a dynamic range of $\sim 10^3$. Absorption coefficients of 895 mm^{-1} and 1.02 mm^{-1} for crude oil and 0.51 g/kg $K_2Cr_2O_7$ standard were measured. The system was accurate to better than 5%.

Pruiksma and McCreery[150] monitored electrogenerated chromophores by a laser absorption spectrometer. Species as close as 10 μm to the electrode surface were monitored.

IV. MOLECULAR LUMINESCENCE SPECTROMETRY

A. General Comments

The majority of laser excited luminescence spectrometry studies of analytical significance have involved fluorimetry. Laser excitation in the past few years has been applied extensively to fluorimetry and very recently to phosphorimetry.

Winefordner[151] has reviewed laser excited atomic and molecular fluorescence, particularly with regard to the analytical uses, and Wehry[152] has also recently reviewed molecular fluorescence and phosphorescence with laser excitation.

Laser excited (atomic or molecular) luminescence spectrometry has several benefits that should be stressed when compared with conventional source luminescence spectrometry: (1) if saturation can be nearly reached, the luminescence signal of the analyte will be weakly dependent upon the sample environment, source intensity, and intensity fluctuation; (2) if saturation can be nearly reached, analytical calibration curves are linear over an even larger dynamic range; (3) spatial and temporal diagnostic measurements can be performed on a given analyte in a given environment, e.g., flames; (4) small samples can be monitored and/or sample surfaces can be studied as a function of position; and (5) fluorescence probes and laser saturated fluorescence can result in single species detection in certain specific cases and in sub ppb detection limits in most analytical situations.

A typical laser fluorimetric system is shown in schematic fashion in Figure 2a when a flame or a furnace cell is used as the sample compartment. Although all of the fluorescence studies to be discussed here involve electronic transitions in the uv visible spectral region, fluorescence transitions can (and do) involve vibrational transitions in the ir region. In the former case, CW Ar^+ (or Kr^+) pumped dye lasers or pulsed N_2-dye lasers, flashlamp pumped dye lasers, and Nd-YAG pumped dye lasers are the primary sources, but in the latter, CO_2/CO gas lasers could be used. In all of the studies below, only electronic fluorescence will be of concern.

B. Condensed Phase Fluorimetry — Direct Analysis

The analytical application of laser excited fluorimetry (in 1974) for molecules in the condensed phase was done by Smith et al.[153] These workers showed that N_2-pumped dye laser excitation resulted in near saturation conditions for several molecules (fluorescein, acridine, and quinine) and obtained sub ppb detection limits (≈0.01 ppb) for these molecules. Prior to the Smith et al.[153] work, Vickers et al.[154] determined CW laser excited (Ar^+) Raman and fluorescence spectra of several pesticides and indicated the possibility of monitoring pesticide levels in the environment; the authors are aware of no further work.

In 1974, LeBlanc et al.[155] observed weak fluorescence of chlorophylls excited by a He-Ne or a He-Cd laser. They obtained a detection limit for chlorophyll a or b of the order of 10^{-12} *M*. However, these authors were primarily concerned with the use of the laser spectrofluorimeter for structural studies as well as energy transfer studies in biological membranes.

Harrington and Malmstadt[156] described, in early 1975, a single modified monochromator both as a tunable dye laser source of excitation and as a scanning monochromator for emission fluorescence spectra. The unique design, which simultaneously used one monochromator in the dual role of wavelength selectable, narrow band excitation source and as the dispersive spectrometer for fluorescent emission spectra, was designed from a low cost commercial monochromator and an easily constructable N_2-laser. Fluorescence spectra were obtained from low concentrations with this system. A linear analytical calibration curve was obtained from 10^{-7} to 2×10^{-9} *M* fluorescein (detection limit ≈0.08 ng/mℓ). By means of the use of one or several nanosecond pulses, no sample photodecomposition occurred. Pulse-to-pulse fluorescence variation was between 1 to 6% RSD at all concentrations.

Several other groups of workers used a pulsed N_2 laser-dye laser fluorimeter approach. These groups include Van Geel and Winefordner,[157] Richardson et al.,[158-160] Bradley and Zare,[161] Imasaka et al.,[162,163] Ishibashi et al.,[164] and Campen and Bachman.[165] In all of these cases, the systems were basically the same; the N_2-laser power varied from 100 to 1000 kW. Sub-ppb detection limits (in many cases) were obtained for a variety of molecules (Table 4). Richardson and George[160] compared three laser excitation systems: N_2-pumped dye laser, cavity dumped Ar^+ laser, and externally pulsed picked mode-locked Ar^+ ion laser using Rhodamine B as the fluorophor probe in all three cases. Detection limits for the three systems were 1.0, 0.5, and 15 ppb, respectively. Although

Table 4
DETECTION LIMITS (ng/mℓ) OF CONDENSED PHASE MOLECULES BY LASER SPECTROMETRY

Species	Method[a]	Laser[a]	Detection limit (ng/mℓ)	Ref.
Acridine yellow	MF	CD-Ar^+	6	178
Acridine red	MF	CD-Ar^+	0.8	178
Acridine	MF	N_2-laser	0.005	158
Acridine	MF	N_2-dye	0.3	154
Aflatoxins (B_1,B_2,G_1,G_2)	MF	He-Cd	0.006	166
Aflatoxins (B_1,G_1)	MF	N_2laser	3	161
Anthracene	MF	N_2-dye	0.004	160
Anthracene	MF	N_2-laser	0.01	158
BBO[b]	2MF	Ar^+	310	179
Benz(a)anthracene	MF(MI)	N_2-dye	30 pg	171
Benzene	MF	N_2-dye	19	160
Benzo(a)pyrene	MF(MI)	N_2-dye	0.4 pg	171
Benzo(k)fluoranthene	MF(MI)	N_2-dye	0.4 pg	171
Chlorophyll[a or b]	MF	He/Cd	0.001	156
Chrysene	MF	N_2-laser	0.03	158
Cu-EDTA	TL	He-Ne	1000	108
2,5 Diphenloxazole	2MF	Ar^+-dye	100	180
DMPOPOP[c]	MF	CD-Ar^+	110	180
Fluoranthene	MF	N_2-dye	0.001	160
Fluoranthene	MF	N_2-laser	0.01	158
Fluorescein	MF	N_2-laser	0.03	158
Fluorescein	MF	N_2-dye	0.002	162
Fluorescein	MF	N_2-dye	0.08	157
Fluorescein	MF	N_2-dye	0.02	154
Fluorescein	MF	N_2-dye	0.01; 0.00002	163, 164
Glucose-6-phosphate	MF(EA)	He-Cd	2×10^{-12} mol (2 nM)	169
Insulin	MF(FIA)	Ar^+	0.4	168
α-Ketogutaric acid	MF(EA)	He-Cd	4×10^{-12} mol (4 nM)	169
NADP[d]	MF(EA)	He-Cd	10^{-14} mol	169
Naphtalene	MF	N_2-dye	0.001	160
Nitrate	IR	Ar^+-dye	$\approx 10^{-3}$ *M*	244
NPO[e]	MF	CD-Ar^+	100	180
PBD[f]	2 MF	Ar^+	90	179
Phenanthrene	MF	N_2-laser	0.05	158
Phenol	RR	Ar^+	20	228
PPO[g]	2 MF	Ar^+	1500	179
Polyethyleneimine (fluorescein tag)	MF		(1 molecule)	181
Pyrene	MF	N_2-dye	0.0005	160
Pyrene	MF	N_2-laser	0.02	158
Quinine	MF	N_2-laser	0.01	158
Quinine	MF	N_2-dye	0.01	154
Rare earth ions[h]	MF	N_2-dye	0.0006—0.5	50
Rhodamine 6G	MF	N_2-laser	0.0006	161
Rhodamine B	MF	N_2-dye	0.001	160
Rhodamine B	MF	CD-Ar^+	0.1	180
Riboflavin	MF	N_2-dye	0.001	159
Riboflavin	MF	N_2-dye	0.0006	164
Rose Bengal	MF	CD-Ar^+	0.8	178
Rubrene	MF	CD-Ar^+	0.5	178
p-Terphenyl	2 MF	Ar^+-dye	46	180
Tryptophan	MF	CD-Ar^+	2400	180

Table 4 (continued)
DETECTION LIMITS (ng/mℓ) OF CONDENSED PHASE MOLECULES BY LASER SPECTROMETRY

Species	Method[a]	Laser[a]	Detection limit (ng/mℓ)	Ref.
UO_2^+	MF	?	0.05	165
Zearalenone	MF	He-Cd	5	170

[a] MF = molecular fluorescence; 2 MF = two-photon excited molecular fluorescence; MF(MI) = molecular fluorescence (matrix isolation); TL = thermal lensing; MF(EA) = molecular fluorescence (enzyme amplification); MF(FIA) = molecular fluorescence (fluorescence immunoassay); IR = inverse Raman; RR = resonance Raman; CD-Ar^+ = cavity dumped argon ion laser.

[b] 2,5-Di(p-diphenyl)-oxazole.

[c] 1,4 Bis-2-(4-methyl-5-phenoxazolyl)benzene.

[d] Nicotinamide-adenine-dinucleotide-phosphate.

[e] 2-(1-Naphthyl)-5-phenyloxazole.

[f] 2-Phenyl-5(4-biphenylyl)-1,3,4 oxazole.

[g] 2-5 Diphenyl oxazole.

[h] In CaF_2 precipitate.

the first two excitation techniques were equivalent, the N_2-pumped dye laser was considered the most flexible and generally the most applicable laser system for trace analysis. The cavity dumped ion laser had only a few lines for use; a dye laser could have been used with it but with a power loss and frequency spread reduction. The N_2-pumped dye laser has a wide wavelength range (213 to 950 nm) with good peak power at all wavelengths ($\gtrsim$1 kW). A synchronously pumped dye laser could be an alternative approach but was not tested. Imasaka et al.[163] used a N_2-dye laser source with a gated photon counter for time-resolved fluorescence of fluorescein in water and atmosphere NO_2. The same authors[163] obtained "world record" detection limits of 0.02 and 0.6 ppt for fluorescein and riboflavin using the same experimental system. Campen and Bachmann[165] used laser-induced fluorescence for the direct analysis of trace levels of uranium in ground, surface, and ocean water. These authors found a detection limit of 50 ppt for uranium, which was better than all previously used analytical methods.

A clever means of maximizing the laser flux in the smallest amount of sample was developed by Zare and co-workers.[166,167] The eluent from a chromatograph issued as a drop which flowed down the outside of a solid rod. Thus, the cell consisted of a 4-μℓ drop with no windows. The laser source was an amplitude modulated He-Cd ion laser. A detection limit for aflatoxins was 0.75 pg. For aflatoxin B, in corn, a method was developed using both thin layer chromatography and high performance liquid chromatography followed by laser fluorimetry. Aflatoxin B, at 0.1 ppb, could be determined with a relative standard deviation of 26%.

Moreover, Zare and co-workers[168-170] have developed several unique approaches to measurement of species of biological importance via laser-induced fluorescence. By means of fluorescence immunoassay,[168] with a CW Ar ion laser, a detection limit of 0.4 ng/mℓ was obtained for insulin; the bound and free fluorescent-labelled antigens were separated by high pressure liquid chromatography prior to laser fluorimetry. Fluorescein isothiocyanate served as the fluorescent tag.

Imasaka and Zare[169] have applied laser fluorimetry to the detection of enzyme reaction products at extremely low concentrations using the 325 nm He-Cd laser line and liquid filters to isolate the fluorescence. Two direct enzyme reactions permitted quantitation of glucose-6-phosphate with a detection limit of 2 nM and α-ketoglutaric acid with a detection limit of 4 pmol. By combining the two enzyme reactions, 0.01 pmol of NADP was detected; this detection limit is ≈30 times better than the best previously reported. By combining high pressure liquid chromatography and laser fluorimetry, Diebold et al.[170] were able to detect and quantitate the mycotoxin and zearalenone in contaminated corn. Linear fluorescence response occurred over four orders of magnitude and a detection limit of 5 ppb was obtained.

Wehry et al.[171,172] have demonstrated the analytical utility of laser induced fluorescence of polycyclic aromatic hydrocarbons matrix isolated in vapor-deposited, annealed n-heptane deposits (at 4 K). Extremely good spectral selectivity was obtained (over inert gas matrices). The usefulness of this approach to the analysis of complex multicomponent mixtures, such as coking plant water fractions, was shown. Analytical calibration curves were linear from about 30 pg (detection limit) to over 3 μg for benz(a)anthracene with benzo(b)fluorene as an internal standard. Detection limits of benzo(k)fluoranthene and benzo(a)pyrene were about 400 fg. Fingerprinting of incompletely separated constituents in complex samples appears to be a possibility.

Matthews and Lytle[173] have shown that solvent scatter and luminescence are the major background limitations in laser excited solution luminescence spectrometry. The background can be reduced either by solvent purification, by temporal resolution, or by spectral resolution. Richardson et al.[174] have used a novel two-laser (cw Ar ion and cw CO_2 lasers) induced selective ir-visible fluoresence system for thin film analysis. The two laser excitation approach gave increased selectivity.

Eastman[175] described a clever light scattering method to calibrate the intensity of fluorescence; a colloidal solution appears to be a suitable fluorescence standard.

One of the major limiting factors in organic fluorimetry is the "huge" breadth of the emission bands, which results in many potential spectral intereferences in any analytical measurement. Selectivity can, of course, be enhanced by using temporal resolution or matrix isolation methods of immersing the analyte in a host PAH crystal, in a Shpolskii solvent, or in an inert gas matrix. The use of temporal resolution is a viable approach and should be attempted more often in routine analytical studies.[177] In the matrix isolation case, the methods based upon a host PAH crystal and an inert gas matrix are both time consuming and tedious. The Shpolskii matrix approach is more viable, but the relative intensities of the spectral components depend upon cooling rate.

An extremely exciting paper has been written by Brown et al.[176] who describe a method based on fluorescence line narrowing spectrometry in organic glasses for detection of ppb of polycyclic aromatic hydrocarbons. They chose an alternative solid state approach by using organic glasses for the PAHs. By means of narrow line laser excitation and placing the PAHs in organic glasses at ~4 K, fluorescence line narrowing of the PAHs occurs, i.e., the peaks were ≈10 cm^{-1} in halfwidth as opposed to ≈200 cm^{-1} when conventional solvents with laser excitation is used. The system used by Brown et al.[176] consisted of an Ar^+ laser (no saturation effects), thin-walled plastic tubes for the samples, a liquid He-cryostat, a large aperture monochromator, and a photomultiplier detector. Selective excitation as well as selective measurement of fluorescence greatly simplify the analysis of complex mixtures. Detection limits in the sub-ppb range were obtained for pyrene and anthracene. The use of a N_2-pumped dye laser, gated detection, and an intensified image detector could greatly increase the analytical potential of this system. In addition, temporal resolution could increase even more the informing power of this powerful technique.

Lytle and Kelsey[178] have used a cavity-dumped Ar^+ ion laser as an excitation source for time resolved fluorimetry. The system had the following characteristics: repetition rate —

single-shot to 10 MHz; variable pulse width — CW to 9 ns; and moderate peak power — ≈1 to 12 W. Detection limits of ~10^{-6} *M* to 10^{-9} *M* for a variety of organic molecules were obtained. By using a photon counting technique, extending the wavelength coverage of the laser by use of a Kr^+ ion laser and frequency doubling crystals, and by a combination of mode locking, it should be possible (according to the authors) to improve the detection limit from the ppb to the ppt range.

Two-photon excited fluorescence studies have been described by two groups. Sepaniak and Young[179] used a two-photon excited fluorescence detector for liquid chromatography. They used the 514.5 nm line of an Ar^+ laser. Detection limits for several molecules were in the low to middle ng range. Wirth and Lytle[180a] showed that two-photon absorption with fluorescence detection led to scatter-free results for even optically dense solvents. Linear analytical calibration curves were obtained in all cases from the submicromolar levels to the saturation concentration. In addition to the above advantages, there is also no inner filter effect in two-photon absorption-fluorimetry (optically dense matrices for one photon absorption, e.g., at 257 nm, are often optically thin for two photon absorption, e.g., two photon at 514 nm). Therefore, even though the fluorescence signals are considerably weaker (the two-photon absorption cross section, which is intensity dependent, is orders of magnitude smaller than the one photon absorption cross section, even assuming the use of an intense laser source), the reduced noise (detector noise is often limiting) results in much larger signal to noise ratio (SNR) than one might expect. Finally, bulk excitation can be readily used with two-photon absorption-fluorescence without risk of fluorophor absorption interference on the cell walls in line with the excitation. In their study, Wirth and Lytle[180a] used a synchronously pumped CW dye laser.

C. Condensed Phase Fluorimetry — Biological Applications

Harris[180b] has reviewed the use of tunable lasers for biological studies — primarily fluorescence microscopy.

Hirshfeld[181,182] has discussed the use of fluorescent tagging with laser excitation to detect individual molecules, e.g., between 80 and 100 fluorescein isothiocyanate molecules are bound to one molecule of MW 20,000 polyethyleneimine, which is then bound to one γ-globulin. Excitation was by means of an Ar^+ laser. The sample, 2 $\mu\ell$ at about 10^{-11} *M*, was placed on a microscope slide and mechanically driven in a microphotometer. Photometric peaks were observed for individual γ-globulin molecules. Hirschfeld,[182] in a later paper, considered the sensitivity of biological analysis using fluorescent tagged reagents; the limit of the method is imposed by concentration quenching of the fluorescence of high tag concentrations and by photochemical bleaching due to the high excitation intensities used. It is shown theoretically and experimentally that concentration quenching lengthens bleaching lifetimes and that the integrated fluorescence emission on complete bleaching does not vary with fluorescent quantum efficiency, absorption cross section, and excitation intensity and duration.

Hirschfeld et al.[183,184] have described a virometer which is an optical instrument for visual observation, measurement, and classification of free viruses. The device is based upon fluorescence correlation spectrometry and total reflection fluorescence; by photoelectric detection, viruses are sized at moderate concentrations in biological fluids in minutes. Fluorescence staining methods are used for specific nucleic acids. In this approach, light intensity variations produced in the number of fluorescent stained viruses are measured as they are driven by Brownian motion through a small excitation region. The photometer electronics are adjusted to allow discrimination against fluctuation frequencies characteristic of particles outside this size range. By measuring fluorescence fluctuations, the fluctuation frequency spectrum is independent of the angle of observation as opposed to techniques based upon the Doppler shift. The method has been used for viruses containing nucleic acids which are in the viral size range of ≈20 to 500 nm.

Wright[185] has described an interesting theoretical approach to increasing the selectivity of analysis via fluorimetry. He described the feasibility of performing double resonance excitation of fluorescence from molecules in a condensed phase. The approach is predicted to have the sharp lines characteristic of Raman or ir spectroscopy, but the high sensitivity characteristic of fluorescence spectroscopy.

D. Gas Phase Fluorimetry

Ehrlich and Wilson[186] have observed subnanosecond laser excited fluorescence of pyrene and fluoranthene vapors. Gatterman and Stockburger[187] have observed the two-photon (virtual levels) and multiphoton (real levels) excitation of naphthalene vapor by both excitation and fluorescence spectra. In the latter case, N_2-pumped dye laser pulses were used. Such specra exhibit considerable fine structure when the studies are performed at low pressures. This technique can thus be used as a selective, sensitive gas chromatographic detector. Detection limits are given in Table 5.

Laser induced molecular backgrounds in both gaseous hydrocarbon fueled flames (C_2H_2 per air and C_2H_2/N_2O)[188] and liquid hydrocarbon fueled flames (kerosene per air and gasoline per air)[189] have been reported. In the latter flame, an indication of the presence of polycyclic aromatic hydrocarbons was noted. The observation that the broadband fluorescence observed with an argon ion laser could be attributed to polycyclic aromatic hydrocarbons was made by D'Alessio et al.[189a] early in 1975. The subject has been studied in detail by Coe and Steinfeld,[189b,189c] who used a flash-pumped tunable dye laser and measured the excitation and fluorescence spectra of several individual species in a heated cell and in a flame. Several workers[26,27,190] have also reported on the laser excited molecular fluorescence of species such as BaO, BaOH, BaCl, CaOH, SrOH, CrO, and MnO, resulting from the introduction of a suitable solution of the corresponding element in the flame, as well as native flame species such as CH, C_2, and CN.

The absolute concentration of native flame species, e.g., CH, CN, and OH have been measured by laser induced fluorescence. These techniques generally require saturation to minimize the influence of quenching phenomena (assuming a two-level molecule is involved) and numerous assumptions with regards to the excitation and de-excitation rate constants for molecules which do not obey the two-level energy scheme. The reader is referred to the work of Chan and Daily,[191-193] Bonczyk and Shirley,[194] Lucht and Laurendeau,[195] Berg and Shackleford,[196] Crosley and Smith,[197] and Baronawski and McDonald.[198,199] Several other experimental studies of gas species in flames by laser induced fluorescence include NO in an atmospheric CH_4-O_2-N_2 flame by Grieser and Barnes[200] and OH concentration profile in an atmospheric premixed CH_4-air flame by Bechtel and Teets.[201] Barnes and Kircher[202] have measured NO_2 levels in an atmospheric $CH_4/O_2/N_2$ flame using a N_2-dye laser.

E. Pollution Analysis

Fluorescence detection of laser excited pollutants has been one of the most sensitive methods of analysis, both in remote sensing and in laboratory gas cell measurements. Because the fluorescence cross section for a given analyte gas varies greatly with the environment, it is necessary to calibrate the system for analytical measurements. In the laboratory measurements, this is rather trivial, but in the remote sensing measurements, many problems are encountered. If saturation can be produced in the analyte and if the analyte can be represented as a two energy level molecule (or atom), then the environmental effects are minor.[2,5] However, atmospheric absorption negates the use of

Table 5
DETECTION LIMITS OF GASEOUS MOLECULES BY LASER SPECTROMETRY

Species	Method[a]	Laser[b]	Environment	Cell length (cm)	Detection limit (ppm)	Ref.
Acrylonitrile	Stark,MA	CO_2	Cell, 1 atm, 5 torr	40	0.03	145
Aniline	MA(OA)	FL	Ambient	2	10^{-5}	303
Benzene	MA(OA)	CO_2	Ambient,N_2	13	2	288
CH_4	R(OA)	Nd-YAG-dye	Ambient,N_2	?	2	290
CH_4	MA	DL	Ambient	1,000	14	148
CH_4	MA	DL	Ambient	5,000	0.00003‡	133
C_2H_4	OA	CO_2	Ambient	15	0.0003	283
C_2H_4	MA	DL	Ambient	1,000	0.03	127
C_2H_4	MA	CO_2	Ambient	1,200	0.0005	147
C_2H_4	MA	DL	Ambient	1,000	0.7	129
C_2H_4	MA	DL	Ambient	2,000	0.0008	132
C_2H_4	R(OA)	Nd-YAG-dye	Ambient,N_2	?	4	290
CO	MA	DL	Ambient	1,000	4	148
CO	MA	DL	Ambient	5,000	0.00001‡	133
CO	MA	DL	Ambient	2,000	0.001	132
CO	MA	DL	Flame,1 atm	≈ 1	≈ 1	137
CO_2	MA	DL	Ambient	5,000	0.3	133
CO_2	R(OA)	Nd-YAG-dye	Ambient,N_2	?	2	290
C_2H_3Cl	R(OA)	Nd-YAG-dye	Ambient,N_2	?	9	290
D_2O	OA	CO,CO_2	Ambient,N_2	8.5	0.1	284
Ethanol	MA(OA)	CO_2	Ambient,N_2	13	0.4	288
Ethylene	MA(OA)	CO_2	Ambient,N_2	13	0.05	288
Freon-11	MA	DL	Ambient	1,000	0.3	129
Freon-12	MA	DL	Ambient	100	0.1	129
Freon-12	MA(OA)	CO_2	Ambient,N_2	13	0.1	288
H_2	R	Ar^+	Ambient,N_2	10	<1	237
H_2	CARS	Ruby	N_2-1 atm	≈ 0.5	10—100	250a
H_2O	MA(OA)	CO,CO_2	Ambient,N_2	8.5	0.5	284
H_2O	MA	DL	Ambient	5,000	0.05	133
HDO	OA	CO,CO_2	Ambient,N_2	8.5	1	284
I_2	MF	Ar^+-dye	Quartz cell	5	0.01	72
Methanol	Stark,MA	CO_2	Cell,1 atm, 5 torr	40	0.08	145
Napthalene	MA(OG)	FL	Ambient	5	10^{-6}	302
NH_3	MA	DL	Ambient	1,000	0.03	127
NH_3	MA	DL	Ambient	5,000	0.00005	133
NH_3	MA	DL	Ambient	1,000	0.3	129
NH_3	MA(OA)	CO_2	Ambient,N_2	13	0.03	284
NO	MA(OA)	CO,CO_2	Ambient,N_2	8.5	0.2	284
^{15}NO	MA(OA)	CO,CO_2	Ambient,N_2	8.5	0.1	284
NO	MA(OA)	CO	Ambient	1	0.01	278
NO	MA	DL	Ambient	5,000	0.00003‡	133
NO	MA	DL	Ambient	2,000	0.001	132
NO	MA(OA)	SF	Ambient	?	<0.001	268
NO_2	MA(OA)	FL	Ambient	7	0.004	289
NO_2	STARK	CO_2	N_2-1 atm	?	<1	145
NO_2	MF	N_2-dye	Flame-1 atm	≈ 0.2	<1	200
NO_2	MA	DL	Ambient	5,000	0.00002	133
NO_2	MA	N_2-dye	Smoke	3,500	0.2	119
N_2O	MA	DL	Ambient	1,000	9	148
N_2O	R(OA)	N_2-dye	Ambient,N_2	?	20	290

Table 5 (continued)
DETECTION LIMITS OF GASEOUS MOLECULES BY LASER SPECTROMETRY

Species	Method[a]	Laser[b]	Environment	Cell length (cm)	Detection limit (ppm)	Ref.
N_2O	MA	DL	Ambient	5,000	0.002	133
O_3	MA	DL	Cell,3 torr	30,000	0.005	134
O_3	MA	DL	Ambient	?	0.05	133
O_3	MA	DL	Ambient	5,000	0.005	133
O_3	MA	DL	Ambient	5,000	0.000001‡	133
O_3	MA	DL	Ambient	1,000	1	124
O_3	R(OA)	Nd-YAG-dye	Ambient,N_2	?	10	290
Phosgene	OA	CO,CO_2	Ambient,N_2	8.5	0.06	284
SF_6	MA	DL	Ambient	1,000	0.03	127
SO_2	MA	FL	Ambient	1,000	<0.004	115
SO_2	MA	DL	Ambient	5,000	0.003	133
SO_2	MA	DL	Ambient	2,000	0.01	132
Toluene	MA(OA)	CO_2	Ambient,N_2	13	0.8	288
Trichloroethylene	MA(OA)	CO_2	Ambient,N_2	13	0.5	288
Vinyl chloride	Stark,MA	CO_2	Cell, 1 atm, 5 torr	40	≈0.5	145
Vinyl chloride	MA	DL	Ambient	1,000	3	129
Vinylidene Chloride	Stark,MA	CO_2	Cell, 1 atm, 5 torr	40	≈1	145

[a] OA = optoacoustic detection; OG = optogalvanic detection; MA = molecular absorption; MF = molecular fluorescence; R = Raman spectrometry; Stark = Stark modulation.

[b] CARS = coherent anti-Stokes Raman scatter; CO, CO_2, Ar^+, He/Ne, Ruby, Nd-YAG, N_2-dye = specific lasers; DL = diode laser; FL = flashlamp dye laser; SF = spin flip laser.

wavelength excitation (vacuum uv) of the fluorescence of certain species, which confines measurements to the ir and to the near UV visible regions.[114]

Gelbwachs and Birnbaum[203] have measured the fluorescence of aerosols in the ambient atmosphere using a CW Ar^+ laser to excite fluorescence bands in the spectral region of 560 to 810 nm. This broad band fluorescence is primarily a limitation of LIDAR measurement of pollutants, as also shown by Allegrini and Omenetto.[204] Tucker et al.[205] have used molecular fluorescence to monitor NO_2 levels in real time in the atmosphere. An Ar^+ laser (488 nm) was used. Clyne et al.[206] used a pulsed N_2-pumped dye laser (frequency doubled) to excite the fluorescence of several gaseous molecules, including I_2, SO_2, and OH. Unfortunately, the atmospherically important species, the ClO radical, could not be detected by laser induced fluorescence. Imasaka et al.,[207] using a N_2-pumped dye laser, obtained the fluorescence and phosphorescence spectra of biacetyl and NO_2 in the atmosphere.

Heaps[208] has used a LIDAR fluorescence detector approach to measure OH in the upper atmosphere. Such studies are the key to the chemistry of the atmosphere (catalytic destruction of ozone and aerosol formation).

Measures et al.[114,209,210] have developed an interesting means of fingerprinting environmental materials by laser induced fluorescence decay spectra. The temporal behavior of laser induced fluorescence as a function of wavelength for such materials as crude oils, refined petroleum products, fish oils, and rock and mineral samples is used as a spectral signature. The use of a *fluorescence* decay spectrum is more specific than the normal fluorescence spectrum. The environmental probe is called a *laser fluorosensor*

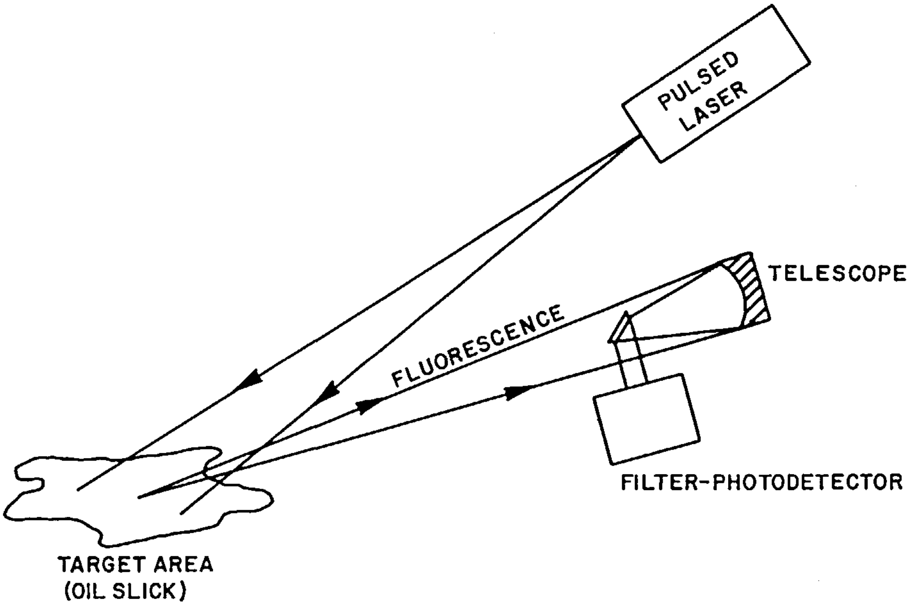

FIGURE 6. Schematic diagram of a typical airborne laser fluorescence system to detect oil spills.

(see Figure 6). An airborne laser fluorosensor was used by O'Neil et al.[211] to detect and identify targets (oil spills) by means of their characteristic fluorescence spectra. A correlation technique was developed capable of clearly differentiating dye fluorescence from two crude oil and general ocean fluorescence. Visser[212] has developed a remote sensing procedure based on fluorescence to determine the thickness of oil films on polluted water. Capelle and Francks[213] have compared an excimer laser (KrF) and a N_2 laser excited fluorosensor system for remote detection of organic effluents associated with coal processing. The systems were evaluated for both daytime and nighttime operation.

F. Condensed Phase Phosphorimetry

Boutilier and Winefordner[214-216] have used a N_2-laser or a Chromatix® flashlamp pumped dye laser to excite organic molecules at 77 K using time resolved measurements with a boxcar averager. The influence of heavy atoms such as I^-, Tl^+, and Ar^+ were evaluated with regard to their effect on both phosphorescence lifetimes and detection limits. The molecules studied included anturange, benzophenone, butazolidine, carbazole, cocaine, codeine, ethylmorphine, morphine, phenanthrene, phenobarbital, phenylcyclidine, procaine, quinine, STP, tanderil, thiopropozate, and vinilblastine sulfate. Generally, the species were found to have both long (seconds) and short (milliseconds) lifetimes, the short lifetime component primarily appearing in the presence of a heavy atom. Also, the phosphorescence signals were considerably greater in the presence of heavy atoms, but the noise levels, particularly with KI added, increased even more, resulting in poorer detection limits in the presence of KI than in its absence ($AgNO_3$ addition generally produced about the same or slightly lower detection limits than in its absence). The solvent used in all cases was 10% ethanol per water (v/v). The detection limits with the N_2 laser (337 nm) were often superior to those with the doubled flashlamp pumped dye laser (270 nm), even when the absorption was much weaker at the 337 nm line; the reasons for this were: (1) the N_2 laser peak power at 337 nm was several

Table 6
DETECTION LIMITS FOR LASER EXCITED CONDENSED PHASE PHOSPHORESCENCE SPECTROMETRY

	Limits of detection (µg/mℓ)					
	N_2-laser			Doubled flashlamp dye laser		
Compound	**E/W**	**E/W/I**	**E/W/Ag**	**E/W**	**E/W/I**	**E/W/Ag**
Anturane	0.03	0.02	—	—[a]	—	—
Benzophenone	0.9	2	0.6	0.2	0.4	0.1
Butazolidin	0.04	0.2	—	—	—	—
Carbazole	0.6	0.3	0.04	—	—	—
Cocaine	0.03	0.06	—	—	—	—
Codeine	0.2	0.9	0.2	—	—	—
Ethyl morphine	0.8	2	0.6	—	—	—
Morphine	1	4	1	—	—	—
Phenanthrene	6	4	2	9	14	0.3
Phencyclidine	0.09	0.04	—	—	—	—
Phenobarbital	0.007	0.01	—	—	—	—
Procaine	0.003	0.01	—	—	—	—
Quinine	2	0.4	0.2	13	9	3
STP	0.008	0.04	—	—	—	—
Thiopropazole	0.002	0.002	0.002	—	—	—
Tandearil	0.1	—	0.05	—	—	—
Vinblastine	0.03	0.07	0.006	—	—	—

Note: Solvent E/W = ethanol/water 10/90 v/v; E/W/I = ethanol/water 10/90/0.75 *M* KI; E/W/Ag = ethanol/water 10/90/0.1 *M* $AgNO_3$.

[a] No results obtained.

From El-Sherbiny, M., Ballik, E. A., Shewchun, J., Garside, B. K., and Reid, J., *Appl. Opt.*, 18, 1198 (1979).

orders of magnitude greater than the doubled flashlamp laser at 270 nm; (2) the N_2 laser was much more stable than the flashlamp dye laser (~0.5% RSD vs. ~6% RSD) due to doubling crystal drift and more rapid dye degradation in the latter case; and (3) because of the above factors, the background noise level was much less with the N_2 laser system. Detection limits are reported in Table 6.

G. Combustion Diagnostics

The importance of evaluating fundamental parameters such as the absolute concentration of species and the temperature of flames and plasmas in order to understand the chemistry of combustion is well recognized. Most conventional diagnostic methods were based upon the use of stainless steel or silica probes inserted into the system and coupled with measuring techniques such as gas chromatography, mass spectroscopy, etc. However, it is essential to be able to probe the system in a nonintrusive way, with both spatial and temporal resolution, especially when strong inhomogeneities exist in the plasma composition and temperature.

Most laser spectroscopic methods discussed in the previous chapters and the Raman techniques described in Section V represent the ideal solution in the field of combustion diagnostics, being capable of providing locally resolved values of the physical parameters characterizing the combustion process. Unlike conventional absorption and emission measurements, the fluorescence and Raman techniques are inherently capable of high

Table 7
RAMAN SPECTROSCOPIC METHODS

Method	Susceptibility[a]
Conventional spontaneous Raman spectrometry	1st Order
Resonance Raman spectrometry	1st Order
Near resonance Raman spectrometry	1st Order
Inverse and AC coupled inverse Raman spectrometry	2nd Order
Raman induced Kerr effect spectrometry (RIKES)	3rd Order
Coherent anti-Stokes Raman spectrometry (CARS)	3rd Order

[a] $P = \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots$; P = polarization; E = electric field strength; $\chi^{(1)}$ = 1st order coefficient (susceptibility); $\chi^{(2)}$ = 2nd order coefficient (1st nonlinear coefficient, which is responsible for second harmonic generation) (susceptibility); $\chi^{(3)}$ = 3rd order coefficient (2nd nonlinear coefficient, which is responsible for third harmonic generation) (susceptibility).

spatial resolution, because only the volume increment at the intersection of the excitation beam and the optical path of the detector is sampled.

The number of papers already published and still appearing in this field is impressive. Although some of the work done in flames has been already mentioned here,[191-202] it was considered somewhat out of the scope of this report to deal extensively with this topic. The reader is therefore referred to the rather comprehensive book by Crosley[216a] in which all the laser techniques described here are shown to be ideally suitable for probing the combustion process.

V. RAMAN SPECTROMETRY

A. General Comments

In Raman spectrometry, laser sources are now used almost exclusively rather than the old mercury arc excitation lamps. The reader is referred to the extensive literature on Raman spectrometry[217-220] for a discussion of its principles, instrumentation, and uses. In this review, only the recent advances involving the use of lasers will be given.

B. Types of Raman Processes

Conventional spontaneous Raman spectroscopy has been found to have considerable use for both qualitative and quantitative analyses, particularly as a complement to infrared absorption spectrometry. Certain symmetrical vibrational modes which are only weakly allowed in the ir spectrum are intense in the Raman spectrum. Other advantages of conventional Raman spectrometry over ir absorption spectrometry include: ease of sample handling; use of aqueous solutions and, therefore, its obvious use in biological applications; and its potential for spatial diagnostical studies. However, the conventional Raman effect is very weak, typically one photon being scattered for every 10^8 to 10^9 incident upon the molecule. In addition, the collection efficiency for conventional isotropic Raman is low, and laser induced fluorescence is often a very serious spectral interference. Some of these limitations can be minimized or eliminated by the Raman techniques listed in Table 7. The last three types of Raman methods involve nonlinear Raman effects. The first three Raman methods involve conventional Raman scattering, i.e., the signal depends upon the first order coefficient (proportional to the electric field strength, E). Both Stokes and anti-Stokes inelastic scattering occur when radiation interacts with molecules; however, for anti-Stokes scattering, the molecules must be already excited or the Raman scattering will be extremely weak even if a laser source is used. As the intensity of the (laser) source is increased, stimulated Raman emission occurs, i.e., the excitation energy is siphoned into only a few intense vibrational modes. Stimulated Raman emission, SRE, only occurs if the concentration of species and the laser flux is high enough and, as a result, has little analytical use.

The *Resonance* and *Near Resonance Raman Effects* (RRE and NRRE) are considerably more intense. For molecules having a strong electronic absorption in the region of laser excitation, Raman scattering of certain vibrational modes may increase by up to $\sim 10^6$X. Of course, for RRE or NRRE, the laser must have its radiant output "in" or "near" the absorption band. NRRE has the additional advantage that the Raman gain is still $\sim 10^6$X (gain in Raman cross section), but fluorescence interference is much less.

The *Inverse Raman Effect* (IRE) has not been greatly used for analytical studies. The IRE results when two laser beams are used, one fixed in wavelength and monochromatic and the other variable in wavelength. As both beams pass through the sample cell, absorption of the short wavelength tunable laser is monitored at frequencies corresponding to the anti-Stokes resonances. The IRE is not very sensitive but does avoid any fluorescence background interference since measurements are made at the shorter wavelength.

The *AC Coupled Inverse Raman Effect* (ACIRE) appears to have considerably more potential for trace quantitative analysis, especially as a gc or lc detector. The ACIRE method is a background free, coherent Raman method in which the absorption in a sample from a laser beam at frequency ν_1 is induced by interaction with a second laser at a laser frequency ν_2. Absorption occurs when $\nu_1 - \nu_2 = \nu_R$, where ν_R is the frequency of a Raman active vibration. Either the Raman gain or loss can be measured. In the AC method, the Raman gain is measured.

Hyper Raman Spectroscopy (HRS) involves Stokes shifted photons with respect to the second harmonic of the exciting laser. However, since hyper Raman scatter occurs over 4π sr, it is not very sensitive and has had little analytical use.

Raman Induced Kerr Effect Spectroscopy (RIKES) is also a third order nonlinear method which requires two lasers. One is a narrow band, fixed wavelength and the other is broad band and fixed or narrow band and tunable. For the broad band case (called the probe), the probe beam is blocked by an analyzing polarizer oriented normal to the polarization direction of the (pump) beam. When the pump beam enters the sample cell, the probe beam transmission through the analyzer at both the Stokes and anti-Stokes frequencies corresponding to the frequency difference between the two laser beams is increased via RIKES. If the pump beam is circularly polarized, background transmission due to the nonresonant Kerr effect is reduced. For liquid and solids, only a few kilowatts of laser power in each beam is needed, whereas for gases much higher fluxes are needed. The success of this method depends upon how efficient laser polarization is and how high the rejection ratio is for the polarizers. This technique has not yet been used for analytical purposes.

The most analytically used, nonlinear Raman method has been CARS, which like RIKES, requires two lasers, one fixed and narrow in frequency and the other variable and narrow in frequency. CARS (Figure 7), unlike spontaneous Raman, produces a coherent laser-like beam in the anti-Stokes region which allows discrimination against fluorescence and allows efficient collection of the Raman scattered light. In CARS, when the frequency of the (higher frequency) fixed laser, ν_ℓ, and the frequency of the (lower frequency) variable laser, ν_s, satisfy $\nu_{as} = 2\nu_\ell - \nu_s$, where ν_{as} is the anti-Stokes frequency, then intense, coherent Raman scattering occurs at an anti-Stokes frequency. CARS is a very efficient process (as much as 1%, compared to 10^{-5}% for spontaneous Raman, of the incident radiation is converted to Raman scatter), is directional, allowing efficient

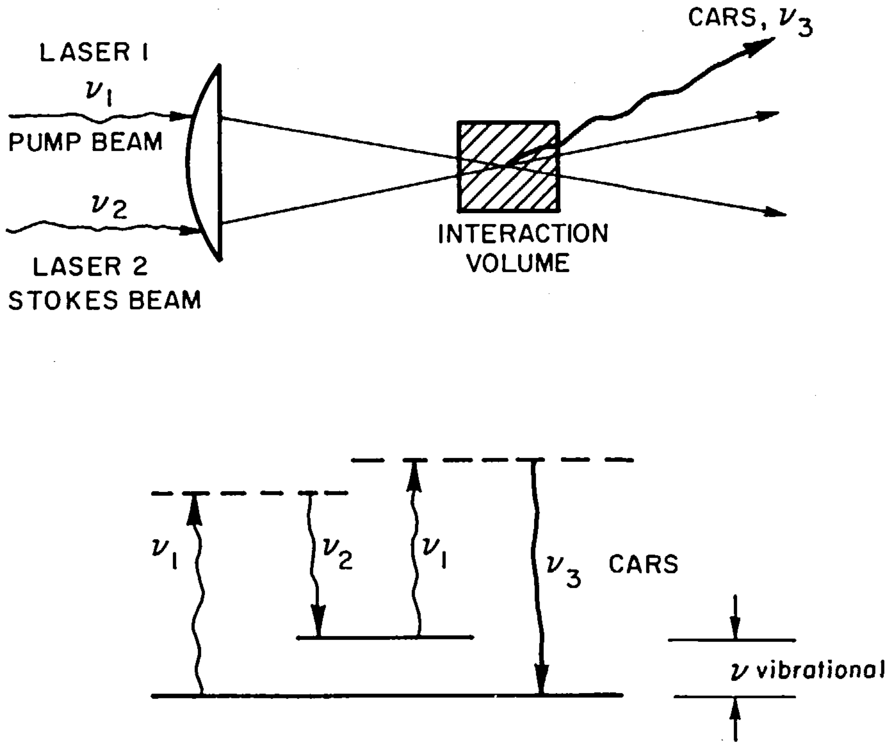

FIGURE 7. Simplified scheme and energy level diagram of the CARS process.

collection, is anti-Stokes, allowing rejection of fluorescence, and is narrow ($\approx$0.03 cm^{-1}), allowing selective measurement. However, CARS is plagued with a nonresonant background which limits detection to about 10,000 ppm in the liquid phase and about 10 ppm in the gas phase. In addition, the CARS signal, like the other nonlinear methods, does not vary with analyte concentration to the first power (for CARS, it is a second power relationship). Finally CARS, RIKES, etc., require high power lasers which are expensive are not commercially available as packaged systems, and can result in sample damage. An excellent discussion of coherent Raman spectroscopy, including CARS and RIKES, is given by Eesley.[221]

Figure 8 summarizes the different nonlinear Raman processes described above. Figure 9 shows two simplified experimental arrangements for the detection of CARS radiation.

C. Applications of Laser Raman Spectroscopy

1. Spontaneous Raman Spectrometry

The uses of laser excitation in spontaneous Raman spectrometry are extensive; the reader can refer to previous reports.[217-220] However, here only certain selected references will be given where novel uses of lasers have been put forth.

McNice,[222] in 1972, showed that the expensive double (or triple) monochromator could be avoided by using a CW tunable dye laser and an interference filter stack in place of the monochromator. By scanning the laser wavelength, a Raman spectrum was obtained. The major restrictions of this device was the extensive scatter and narrow wavelength range of the dye laser used. With wide wavelength range, narrow band dye lasers, the last restriction is now removed, and with improved interference filters, the former restriction is not as severe. This method deserves to be "revisited".

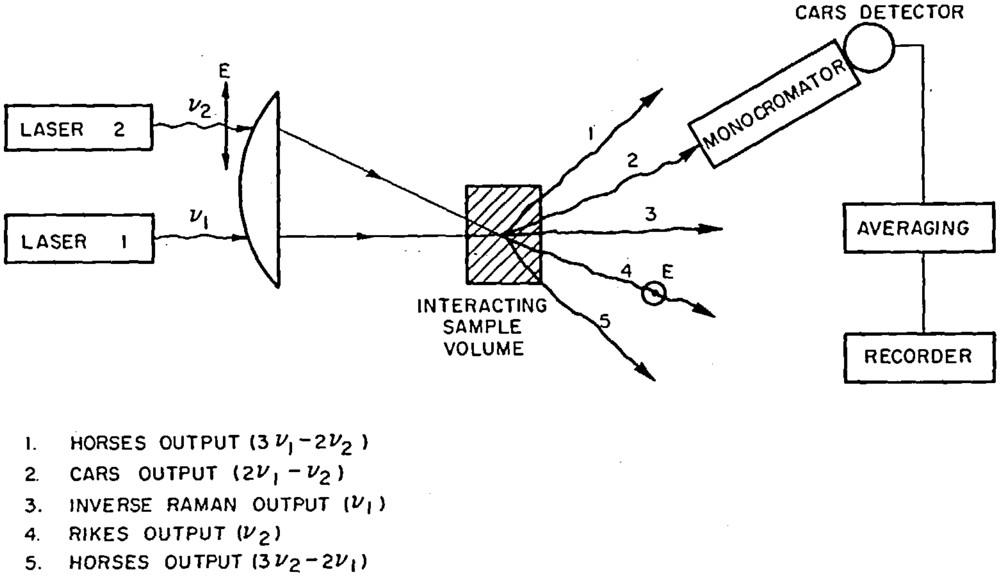

FIGURE 8. Simplified diagram showing the various nonlinear Raman outputs occurring when the two laser frequencies are properly focused into a sample. Note that the electric field vector for the RIKES output is polarized normal to the beam. (Redrawn from Levenson, M. D., *Phys. Today*, 44 (1977).

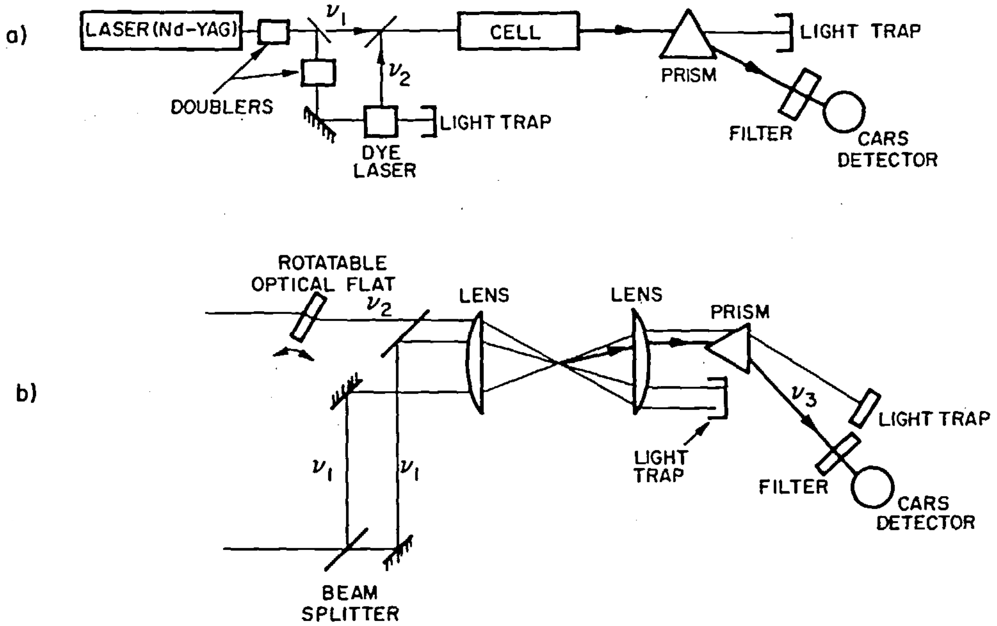

FIGURE 9. Simplified block diagrams for the experimental detection of CARS signals. (a) Co-linear phase matching; (b) crossed-beam phase matching (BOXCARS). (Adapted from Eckbreth, A. C., Bonczyk, P. A., and Shirley, J. A., EPA-600/7/78-104, June 1978.)

Cunningham et al.[223] have evaluated the influence of experimental parameters on detection sensitivity for laser Raman analysis of dissolved solutes, as nitrate, phosphate, monohydrogen phosphate, dihydrogen phosphate, acetate, sulfate, carbonate, bicarbonate, and acetic acid, and have derived an expression for the signal-to-noise ratio in terms of solute concentration, measurement time, spectral bandwidth, laser power fluctuations, and solvent background. For a SNR of 2 and a 5-min measurement time, detection limits between 1 and 10 μg/mℓ result for such anions.

Bell and Tyte[224] were one of the first groups to evaluate the use of a pulsed dye laser and gated photon counting synchronized to the laser pulses; this system allowed efficient rejection of fluorescence in the measurement of Raman scatter and the efficient measurement of fluorescence in the absence of Raman scatter.

Kato[225] has described a versatile Raman spectrometer for fast and reliable isotopic analysis. Deuterium in a mixture of H_2O and D_2O was analyzed. The detection limit of deuterium was under 1 mol %.

2. *Resonance and Near Resonance Raman Spectrometry*

Near resonant Raman spectrometry has not been used for analytical studies despite its obvious advantages over resonance and spontaneous Raman methods. It has been used for studies of gases, but primarily with regard to spectral and temporal features.

Resonance Raman spectrometry has found some use for "trace" analysis. Hoskins and Alexander[226] have used this method for determining the concentration of carotenoids in acetone extracts of marine phytoplankton and obtained estimated errors of about 10% and detection limits of the order of 10^{-8} *M*. No chemical interferences were obtained, and so no physical separations were necessary. Estimated resonance Raman cross sections are given in Table 8.

Van Haverbeke et al.[227] have measured industrial fabric dyes in distilled water at concentrations below 0.2 ppm using resonance Raman spectrometry; the detection limits were of the order of 0.1 ppm. Industrial dyes were identified and quantified in doped river and seawater samples. Van Haverbeke and Herman[228] have also determined three phenolic compounds in water by laser excited resonance Raman; a detection limit of 20 ppb for phenol was obtained; the detection limit for phenol in natural waters was 50 to 300 ppb.

Resonance Raman spectrometry has been used to determine catecholamines[229] at the $10^{-5}M$ level in synthetic mixtures of adrenaline, noradrenaline, dopamine, and isoproterenol without physical separation. Rahman and Morris[230] also report the use of resonance Raman for determining concentrations of adrenaline and noradrenaline (as the aminochromes) as low as 10^{-6} *M*. Resonance Raman[231] has also been used for structural studies involving spectroelectrochemistry.

Harris et al.[232] have improved the signal-to-noise ratios and thus the detection limits of spontaneous Raman spectrometry by using subnanosecond time resolution to reject fluorescence background. Because of the huge difference in cross sections for Raman and fluorescence, the unwanted fluorescence background and concomitant noise generally limits spontaneous Raman detection limits. By using time resolution, i.e., measuring only the emitted-scattered photons during the first few hundred picoseconds produced by a mode-locked cavity dumped argon ion laser, the measured signal consisted mainly of Raman rather than the longer-lived fluorescence. By such measurement, detection limits in the micromolar to nanomolar level are feasible.

Woodruff and Farquharson[233] have used time resolved resonance Raman spectrometry to obtain the Raman spectrum of cytochrome c in dilute (5.5×10^{-4} *M*) solution excited by a single 7 ns laser pulse.

Funfschilling and Williams[234] have used wavelength modulation of the exciting radiation from an Ar^+ dye laser to detect micromolar concentrations of chlorophyll in methyltetrahydrofuran at 10 K (site selection). Wavelength modulation allows efficient discrimination of the sharp Raman bands over the broad fluorescence bands. Time resolution and use of a mode locked, cavity dumped laser would have given a further improvement in detection limits.

Table 8
RAMAN SCATTERING DIFFERENTIAL CROSS SECTIONS

Resonance Raman Cross Sections

Molecule	Electronic transition	Vibrational transition	Laser (nm)	Calculated $\frac{d\sigma}{d\Omega}$ (cm^{2}sr^{-1})
CO^+	$A^2\Pi_i - X^2\Sigma^+$	0—1, 1—1	491.3	2.5×10^{-20}
SO	$A^3\Pi_O - X^3\Sigma^+$	0—2, 2—0	257.9	1.3×10^{-20}
OH	$A^2\Sigma^+ - X^3\Pi_i$	0—0, 0—1	306.4	2.4×10^{-22}
NO	$A^2\Sigma^+ - X^2\Pi$	0—0, 0—3	226.2	1.3×10^{-23}
I_2	$B^3\Pi^+_{Ou} - X^1\Sigma^+_g$	0—25, 25—1	546.6	1.2×10^{-24}
SO_2	$\tilde{A}(^1B_1) - \tilde{X}^1A_1$		300.0	1×10^{-24}[a]
^{79}Br-^{81}Br	$B^3\Pi^+_{Ou} - X^1\Sigma^+_g$	0—28, 28—1	526.4	7.8×10^{-27}
NO_2	$\tilde{A}(^2B_1) - \tilde{X}^2A_1$		454.7	5.6×10^{-27}[a]
CO	$a^3\Pi - X^1\Sigma^+$	0—0, 0—1	206.3	4.5×10^{-30}
Cl_2	$A^3\Pi^+_{Ou} - X^1\Sigma^+_g$	0—15, 15—3	493.3	7.1×10^{-31}

Raman Cross Sections at Several Laser Wavelengths

	Vibrational $\frac{d\sigma}{d\Omega}$			Rotational $\frac{d\sigma}{d\Omega}$
	337.1 nm[b]	532.0 nm[b]	488.0 nm[b]	
N_2	3.5×10^{-30}	0.46×10^{-30}	0.68×10^{-30}	5.4×10^{-30}
	2.8×10^{-30}(Q)	1.32×10^{-30}(Q)	1.32×10^{-30}	2×10^{-30}
H_2	—	—	0.88×10^{-30}(Q)	—
O_2	4.6×10^{-30}	0.65×10^{-30}	0.72×10^{-30}	14×10^{-30}
	3.3×10^{-30}(Q)	0.47×10^{-30}	—	—
NO	1.5×10^{-30}	0.2×10^{-30}	0.15×10^{-30}	—
NO_2	ν_1 51×10^{-30}	7.37×10^{-30}	—	—
	ν_2 24×10^{-30}	3.63×10^{-30}	—	—
NH_3	11×10^{-30}	1.3×10^{-30}	2.75×10^{-30}	—
CO	3.6×10^{-30}	0.48×10^{-30}	—	—
CO_2	ν_1 4.2×10^{-30}	0.6×10^{-30}	0.77×10^{-30}	53×10^{-30}
	ν_2 3.1×10^{-30}	0.45×10^{-30}	0.49×10^{-30}	—
H_2O	7.8×10^{-30}(Q)	0.9×10^{-30}	1.4×10^{-30}	—
H_2S	19×10^{-30}	2.4×10^{-30}	3.5×10^{-30}	—
SO_2	17×10^{-30}	2.5×10^{-30}	2.9×10^{-30}	—
CH_4	ν_1 21×10^{-30}	2.6×10^{-30}	3.3×10^{-30}	—
	ν_2 14×10^{-30}	1.7×10^{-30}	—	—
C_2H_4	ν_1 16×10^{-30}	1.9×10^{-30}	—	—
	ν_2 5.4×10^{-30}	0.76×10^{-30}	—	—
C_2H_6	ν_{1_3} —	—	0.88×10^{-30}	—
C_6H_6	ν_1 3.0×10^{-30}	3.7×10^{-30}	3.8×10^{-30}	—
	ν_2 4.4×10^{-30}	5.6×10^{-30}	5.0×10^{-30}	—
SF_6	12×10^{-30}	1.8×10^{-30}	—	—
CCl_4	26×10^{-30}	4.0×10^{-30}	—	—

[a] Mean experimentally measured.

[b] Laser wavelength.

From Eckbreth, A. C., Bonczyk, P. A., and Verdieck, J. F., Technical Report R77-952665-6, United Technologies Research Center, East Hartford, Conn., 1977; Eckbreth, A. C., Bonczyk, P. A., and Shirley, J. A., EPA-600/7/78-104, June 1978.

Barrett and Adams[235] have used a focused Ar^+ laser to detect as little as 10^{11} gas molecules per cm^3. Pulse counting and efficient collection optics were used to detect the spontaneous Raman (rotational-vibrational) scatter.

Barrett and Myers[236] have described a unique and clever system to further improve the detection limits of gases. They used a Fabry-Perot® interferometer to detect the periodic Raman rotational spectra of gaseous analytes. The interferometer spacing was adjusted to have a free spectral range equal to the difference in frequency between rotational lines. Thus, the Fabry-Perot interferometer acted as a comb filter for a given periodic Raman spectrum and transmitted nearly *all* of the rotational lines of the analyte species. A focused CW Ar^+ laser was used for excitation of molecules in a region of $\sim 10^{-8}$ cm^3.

Hercher et al.[237] have recently described an efficient intracavity laser Raman spectrometer capable of detecting 30 ppm of H_2 in air. By use of intracavity methods, an intracavity circulating power of 160 W was obtained from a 1-W nominal output Ar^+ laser.

3. *Inverse Raman Spectrometry*

This method was first used in 1964 by Jones and Stoicheff.[238] Absorption measurements are made by means of a two-laser system. The method is not very sensitive but does avoid fluorescence interference. Yeung[239] later improved the sensitivity of the method by substituting a dye laser for the incoherent probe sources previously used. In this technique, the transmittance of the fixed frequency laser is given by

$$T(\ell) = \exp(-K\Phi_p \frac{d\sigma}{d\Omega} n\ell) \qquad (2)$$

where $K = d\sigma/d\Omega$ is the differential cross section ($cm^2 sr^{-1}$), Φ_p is irradiance ($W\ cm^{-2}$) of the dye laser probe (the frequency of the probe is less than the fixed laser frequency), n is the concentration of absorbers (cm^{-3}), ℓ is the absorption path length, and K is a constant including the optical frequencies involved, the index of refraction, and fundamental quantities. The basic problem here is that it is difficult to obtain an induced absorption of more than a few percent even for a very high peak power laser. Thus detection limits have been considerably poorer than with CARS.

Recently, Owyoung and co-workers[240-242] have described a modified inverse Raman and Raman gain experiment where one laser beam is modulated and lock-in detection is used to extract the induced component in the other laser beam. They have reported Raman gains with CW lasers as low as 10^{-7} and have calculated a detection limit in the ppb range. The sensitivity is, however, limited by the low power of CW lasers.

Morris et al.[243] have improved the Owyoung experiment by using a fixed frequency laser (ν_1) and a higher peak power pulsed dye laser (ν_2) to obtain high Raman induced absorption (or by interchanging the laser functions, fairly high Raman gains). The time dependence of the induced absorption or gain is the same as that of the dye laser. By using AC coupled electronics for detection, they measured low absorption (proportional to concentration). Detection limits, in terms of induced absorptions, as small as 5×10^{-5} were measured; these values were limited by electronic noise which could presumably be reduced to allow absorption as small as 10^{-7} to be measured. Therefore, detection limits in the ppb range are certainly feasible. Haushalter et al.[244] have used AC-coupled inverse Raman to detect 2×10^{-3} *M* aqueous nitrate. Noise sources were primarily a result of thermal blooming and light scatter. Detection limits can probably be reduced by another ten times by better tuning and reduced drift.

Levine and Bethea,[245] using a synchronously pumped mode locked dye laser system, improved the S/N ratio by 300 times over previously used cw stimulated Raman gain spectroscopy. By means of this picosecond Raman gain method, the authors predict detection of a monolayer using a pump of 100 MW/cm^2. However, before the approach will gain general use for absorbing substances, the thermal heating background must be minimized.

4. *Raman Induced Kerr Effect Spectrometry (RIKES)*

RIKES has not yet been used as an analytical technique, even though it would appear to have considerable potential. Generally, the uses of polarization in analytical spectrometry has been slow to reach maturity, but would seem to be near to "rebirth".

5. *Coherent Anti-Stokes Raman Scatter Spectrometry (CARS)*

CARS has been the most frequently used nonlinear Raman technique for both analytical and diagnostical purposes.[246-250] CARS has considerable analytical potential because of the high conversion efficiencies, coherency, and fluorescence discrimination capability. It has been used already for concentration measurement of minor species in flames on both a spatial basis[250-252] and a spatial-temporal basis.[253] Although CARS has been used almost exclusively with high peak power, pulsed lasers, it has been used also with CW lasers to detect methane.[254] Unfortunately, CW lasers are not sufficiently powerful to allow low detection limits to be achieved.

CARS has also been found to be a highly sensitive and selective detector for liquid chromatography.[255] A detection limit of 1 ng/mℓ was obtained for trans-β-carotene. Resonance enhanced CARS has been shown by Hudson et al.[256] to be quite sensitive and has been used to study molecules of biological interest.

Tolles and Turner[257] have given an excellent comparison of the analytical capabilities of CARS, spontaneous Raman scatter, and molecular absorption for gas analysis. They concluded: (1) if luminescence is small, then spontaneous Raman scatter is more sensitive than CARS for samples at 1 atm; (2) greater spectral resolution with the same signal-to-noise ratio is possible with CARS compared to spontaneous Raman scatter; and (3) the sensitivity of spontaneous Raman can be made similar to or exceed CARS by multiple pass cells, increased collection efficiency, and time resolution, higher order Raman processes,[258] i.e., HORSES (higher order Raman excitation studies) have also been found to be useful for fairly dilute solutions ($\lesssim 10^{-3}$ *M*).

6. *Raman Microprobe*

The Raman microprobe is a device based on Raman (and fluorescence) effects where microanalysis is possible in polyatomic molecules. The device is called the MOLE (molecular optical light examiner).[259-262] The instrument permits the specific measurement of molecular components and their selective, spatial mapping in a sample. The MOLE has been used or can be used in the areas of geochemistry and geophysics to study rocks, biology, and medicine for in vivo studies, pollution analysis of urban and industrial particulates, solid state components in integrated circuits, corrosion, photochemical and electrochemical processes, and food, paper, and other materials industries. In the MOLE, the sample is placed under an optical microscope stage and is irradiated through a special optics system by a monochromatic laser (at ν_O). The radiation is scattered at ν_O and at the Stokes and anti-Stokes Raman frequencies as well as emitted as fluorescence. The total image of the sample surface can be observed on a projection screen of the microscope in monochromatic light, i.e., images of the Raman scatter (or fluorescence) at specific frequencies can be viewed and thus concentrations of certain molecular species in the sample surface can be mapped. A survey of several applications of the MOLE technique has recently appeared.[263]

Blaha et al.[264] and Rosasco et al.[265-266] have developed an instrument similar to MOLE called a Raman microprobe. This device has been used to characterize individual urban particulates. They found that many of the urban area particulates arose from carbon present in an elemental form that was analogous to polycrystalline carbon. The carbon was traced either to graphitic soot or to an organic contaminant of the particle which could be connected to graphitic soot by exposure to laser radiance.

7. *Pollution Analysis*

As discussed by Measures,[114] Raman spectrometry has been used extensively for remote sensing of pollutants such as SO_2, NO_2, CO_2, H_2S, etc. Raman LIDAR has been used for major constituents in the atmosphere, but has been difficult to use for trace constituents because of the small Raman cross sections. Resonant Raman, however, is expected to have considerable potential for trace pollutant analysis.

Patel[113] has discussed the laser spectroscopic methods for the determination of specific gaseous pollutants. Three general approaches are reviewed, namely, long-path absorption measurements, laser Raman, and optoacoustic detection. The instrumental system is similar to that shown in Figure 5. The laser transmitter typically consists of a high power pulsed laser in the visible or near uv. The pulsed laser output at frequency ν_O is collimated with a telescope and transmitted in the direction of the atmospheric constituents. The weak Raman scattering contains information about the constituents and their concentrations, but the scatter is radiated in 4π steradians and thus a large telescope near the transmitter is needed to collect an appreciable fraction of the Raman scattering. The amount of radiation collected depends upon the distance at which the scatter is located and the size of the telescope. Unlike absorption measurements, the Raman scattering contains information (fingerprints) about all constituents in the scattered volume. The fingerprint is obtained by a frequency analysis of the return signal. A spectrometer is used to minimize spectral interferences. By temporal analysis of the Raman scattering range (distance) information may be obtained. Unfortunately, LIDAR suffers from the small Raman cross sections, and so detection limits are rarely less than 10 ppm at a distance of 100 m. Of course, enhancement of Raman cross sections occurs for resonance (or near resonance) excitation conditions.

The analytical application of LIDAR measurements to several pollutants have been described in the past, and the reader is referred to the monograph by Measures[114] for the pertinent bibliography.

Leonard et al.[267] have described the application of Raman scattering to remote sensing of subsurface water temperature and salinity. Good correlation between theory and experimental results were obtained. Patel[268] has recently reviewed the field of high resolution spectroscopy in the detection of minor constituents in the atmosphere and stratosphere by the use of tunable spin flip Raman lasers.

Numerous fine reviews and research articles have been written on the use of Raman methods for combustion diagnostics. Because this report is primarily concerned with analytical chemistry rather than absolute measurement of flame temperatures and species concentrations, only a few reviews will be designated here. The reader is referred to the book of Lapp and Penney[268a] and to the reviews of Eckbreth et al.,[246-249] Harvey et al.,[220] and to the recent book of Crosley.[216a]

Other interesting studies include: (1) Chabay et al.[269] have measured concentration fluctuations of specific chemical species in mixed gas flow by Fast Fourier Transform analysis of the Raman signal; (2) the measurement[270] of CO_2 concentration and temperature in a CO/air and CH_4/air flames; (3) the use of fiber optic guides[271] as a means of piping CARS signals effectively from the test area to the control center; and (4) a Raman multichannel system described by D'Orazio[272] for on-line identification of gas chromatographic fractions; 10 nℓ of species, which was 5% of the total amount of sample, could be identified and detected.

8. Biological Applications

Laser Raman[273] has been used extensively for structural studies in the area of biology and medicine for simple molecules like amino acids, sugars, nucleotides, etc., for enzymes, metalloproteins, contractile proteins, serum proteins, toxins, polynucleotides, photoreceptors, lipids, natural products like valinomycin, adriamycin, vitamin B_{12}, etc., viruses, and tissues like lens, retina, and skin. However, few quantitative studies (certainly few involving trace analysis) have been conducted. The specific use of CARS for biological studies has been given by Datta et al.[274]

9. Petroleum Fingerprinting

Laser Raman has also been used[275] to fingerprint (identify) fuel oils, kerosenes, lubricating oils, weathered oils, and actual oil spills by spectral matching techniques.

VI. LASER EXCITED OPTOACOUSTIC AND OPTOGALVANIC DETECTION

A. General Comments

In the absorption and fluorescence methods, radiation is detected by light sensitive detectors such as photomultipliers, semiconductive detectors, etc. The optoacoustic and optogalvanic detection approaches differ in that no spectrometer-detector assembly is used, but rather nonselective detectors based upon selective radiative absorption followed by nonradiative quenching in the former and ionization in the latter. The optoacoustic method is essentially a calorimetric method, and the optogalvanic effect is based upon ionization (in the latter case, thermal excitation processes can and do aid the overall ionization process). The optoacoustic effect has been used more generally in analysis, i.e., for both molecular and atomic measurements, whereas the optogalvanic effect has mainly found analytical use for atomic measurement.

B. Optoacoustic Detection

In optoacoustic detection, the temperature change accompanying the absorption of light and nonradiative deactivation is measured via a change in pressure of the gas. Usually the gas is in a closed cell, although pressure changes have been measured also in flames. The detector is a sensitive acoustic microphone (refer to Figure 2 for a schematic diagram of a typical system). The limitation to the smallest measurable absorption is set by noises within the experimental system, such as detector noise. Absorptions as small as 10^{-9} have been measured by this approach, although presumably this limit could be reduced with greater source flux. However, such problems as window absorption, gas turbulence (as in flames or convection in cells), variation in cell gas pressure, etc., must be kept minimal for the most sensitive detection of trace species. The limitations at the upper end of linearity is set by saturation of the optoacoustic signal from the microphone or by a decrease in the intensity of the source flux within the cell. In the former case, the saturation effect can be minimized by use of optical attenuators to maintain linearity of response, whereas in the latter case, nonlinearity is inherent if the optical depth exceeds ≈ 0.05, i.e., absorption coefficient (cm^{-1}) x absorption path length (cm). Optoacoustic detection has been found to be linear over 7 to 8 decades in NO concentration.

Webster[276] has briefly reviewed the optoacoustic effect, the instrumentation, and applications. Patel[113,268] has also reviewed the optoacoustic effect particularly as applied to pollution analysis. Patel and co-workers[281] have done pioneering work in the area of pollution analysis using optoacoustic detection. They used a spin-flip Raman laser as the excitation source and measured NO in air samples. They were able to detect 0.01 ppm NO using a 4-s integration period. Patel[268] has used a spin-flip Raman laser as a source and has obtained high resolution of ground and excited states of molecules and excellent sensitivity, i.e., he was able to measure absorption coefficients as small as 10^{-10} cm^{-1}. The high sensitivity indicates considerable use for detection of minor atmospheric constituents.

Slatkine and co-workers[282,283] have used an intracavity optoacoustic system for trace gas analysis; a tunable CO_2 laser and a resonant optoacoustic cell of novel design with high immunity to window interference and suitable for flow conditions are used. The absorption sensitivity of the system was found to be 10^{-7} cm^{-1} for a 1 Hz detector bandwidth, but by further reduction of laser internal losses, the measureable absorption should be reduceable to 10^{-10} cm^{-1}. The minimum detectable concentration of ethylene in N_2 was 0.5 ppb/$\sqrt{1\ \text{Hz}}$ with a 1 W 10.533 μm CO_2 laser line. The limiting noise, as expected, was found to be instrumental rather than Brownian.

Schnell and Fischer[284] have used optoacoustic detection for phosgene, CCl_2O, and the isotopic species of $H_2{}^{16}O$, $H_2{}^{18}O$, $HD^{16}O$, $D_2{}^{16}O$, $^{14}N^{16}O$, and $^{15}N^{16}O$. The laser was a CO/CO_2 laser. Minimum detectable concentrations were reported to be <0.1 ppm for phosgene, <2 ppm for water, and 0.2 to 2 ppm for NO. The natural abundances of isotopic species were also measured.

Kerr and Atwood,[285] in a rather early paper, described an optoacoustic system, called *spectrophone,* with a CW CO_2 laser, for analysis of CO_2 in N_2; the minimum detectable peak absorption coefficient was ~ 10^{-7} cm^{-1}. Kamm[286] has described a resonant optoacoustic method for trace analysis. The resonant spectrophone was first used by Dewey, Kamm, and Hackett.[287] The advantage of a resonant method lies in the possibility of accumulating energy in a standing acoustic wave which results in signal amplification. Konjevic and Jovicevic[288] described a laser spectrophone to measure the absorption coefficients of seven gas pollutants (atmospheric pressure) at the CO_2 wavelengths of 9.2 μm and 10.8 μm. Kamm[286] presents the theory for the resonant acoustic process for an excitation of known characteristics with emphasis placed on the dissipation process. Multiple pass configurations are also discussed as a means of increasing the absorbed energy. The resonant device is compared to other detection schemes.

Claspy et al.[289] have used a flashlamp pumped dye laser (pulse width ≈ 1 μs, pulse repetition rate ≈ 30 Hz) for detection of NO_2 in the spectral range of 480 to 625 nm. The sensitivity was ≈ 4 ppb/W of laser power. Sibert et al.[290] have described a new method of trace analysis of gases based on pulsed (dye laser) photoacoustic Raman spectrometry. This method has been applied to the analysis of CH_4 in N_2, CO_2 in N_2, and N_2O in N_2 for concentrations near 1 ppm. The method is broadly based covering 0 to 4000 cm^{-1}, and combines the best features of other laser based analytical methods and has considerable advantages over nonlinear Raman methods and ir absorption.

Lahmann et al.[291] have used a frequency modulated beam from an Ar^+ laser (488 and 514 nm) for trace analysis of molecules in the liquid phase. The output was used to excite the sample at a periodically alternating wavelength. By means of dual-wavelength operation (differential absorption), the background signal was considerably reduced and detection limit of $\approx 9 \times 10^{10}$ β-carotene per cm^3 (12 ppt) was obtained (this corresponded to an absorption coefficient of $\approx 10^{-5}$ cm^{-1}). Selenium was also detected by the Se(IV) oxidation product of diphenylhydrazine, namely diphenylhydrazine quinonearyl; a detection limit of 15 ng Se/cm^3 was obtained (corresponding to an absorption coefficient of 3.5×10^{-5} cm^{-1}). Because the method for Se is an indirect approach, a physical separation of certain impurities is needed.

Optoacoustic measurements have also been applied to liquid solutions as well as gaseous solutions. Patel et al.[268,292-297] have applied pulsed dye laser optoacoustic spectroscopy to the weak absorption of benzene ($\approx 10^{-7}$ cm^{-1}), to neat liquids, and to light and heavy water. In addition, two-photon absorption optoacoustic detection[295] has been used to study extremely weak transitions, such as in benzene. Patel and Tam[296] also used two synchronized pulsed dye lasers with gated optoacoustic detection to obtain Raman gain in liquids.

Oda et al.[298-300] have described the analysis of turbid solutions,[298] of rare earth ions in aqueous solutions,[299] and the simultaneous determination of a mixture[300] by laser-induced photoacoustic spectroscopy. In the first study,[298] turbid solutions could be measured at concentrations of about 100 times lower than by turbidimetry. The effect of particle size distribution on both the photoacoustic and the turbidimetric signals was studied. In the second study,[299] the photoacoustic spectra of a number of trivalent rare earth ions in aqueous solution were studied; very weak absorption transitions were detectable. In the third study, binary mixtures of food dyes were measured; the optoacoustic (OAS) signals were additive. The great sensitivity of OAS detection allowed low concentrations of mixtures of dyes to be measured even though conventional absorption spectrometry could not be used.

C. Optogalvanic Effect

As mentioned previously, the optogalvanic effect has been used to study atoms and molecules in gas discharges and flames. By sensing the ion current itself rather than the effect on a space-charged-limited electron current, single ions have been detected under nonanalytical conditions.[301] The mechanism of laser excited optogalvanic flame spectroscopy involves an optical transition (which may be saturated by the laser and one or more thermal steps prior to or after the optical step). Detection limits for 14 elements in aqueous solutions and nebulized into an air/C_2H_2 flame are in the low- to sub-ng/mℓ level (see Table 2), and linearity, as in atomic fluorescence flame spectrometry, extends over more than a 10^3-fold range of concentrations (often approaching 10^6).

Frucholz et al.[302] have described an innovative two-photon photoionization approach to the detection of organic vapors; a frequency doubled flashlamp pumped dye laser excites the molecule in an ambient pressure buffer gas via a two-photon process, and the resulting ionization is detected with an ionization detector (similar to a proportional counter). This technique has not only great selectivity but also a detection limit of 10^7 molecules cm^{-3}; this limit is expected to be lowered by several orders of magnitude. Brophy and Rettner[303] have also described a two-photon ionization spectrometric method but have applied it to atmospheric pollutants with a detection limit of 1 part of aniline per 10^{11} parts atmospheric air ($\sim 10^7$ molecules cm^{-3} for air in a 10 cm path length cell); a N_2-pumped dye laser was used.

Feldman[304] studied the optogalvanic spectra of NH_3, NO_2, H_2, and N_2 in a low pressure, high voltage discharge.

D. Advantages of Optoacoustic and Optogalvanic Detection Over Optical Detection

The major advantages of nonoptical detection include: (1) no need for a spectrometer assembly and so the instrumentation is less expensive, i.e., optical and nonoptical methods require electronic measurement instrumentation and detectors, but only the optical measurement requires a spectrometer (in absorption studies, a spectrometer may or may not be used but in fluorescence studies, a spectrometer or filter to measure the fluorescence is generally needed); (2) scatter processes do not affect the nonoptical methods; (3) the lack of suitable UV lasers is less critical for nonoptical methods since in these cases, one can often use excited lower states; and (4) the nonoptical methods are ideally suited to multiple photon excitation (involving real levels), e.g., in fluorescence detection, the predominant radiative transitions, particularly in large molecules, involve low lying electronic states; thus, multiple excitation of a high level gives only a marginal increase in selectivity, whereas, in the nonoptical detection schemes, multiple excitation produces direct effects from the radiatively excited states. On the negative side, fluorescence detection allows another degree of selectivity not available in the nonoptical methods or in conventional absorption spectrometry. Also, "broad band" interferences, such as the ambient electron-ion background in flames in the optogalvanic effect and the ambient pressure background in cells in the optoacoustic effect, are generally relatively greater than the sources of background for fluorescence and absorption studies.

E. Resonance Ionization Spectroscopy

This technique deserves an independent place in this section because of its appealing feature of being a *single atom detection* technique. Again, laser-induced ionization of the atom occurs, creating a free electron and an ion, which are then detected by using the conventional counting techniques of nuclear physics.

Hurst et al.,[305-306] at Oak Ridge National Laboratory, were the first group to achieve true single atom detection using a laser in 1976. In their experiment, one cesium atom in a background of 10^{19} atoms of argon and 10^{18} molecules of methane was easily detected. Hurst et al.[307] have recently written an extensive review on the theory of resonance ionization spectroscopy (RIS) and the experimental conditions necessary to achieve single atom detection. According to these authors, several schemes (see Figure 10) can be used to carry out a resonance ionization process. The choice of any of the schemes reported will depend upon the atom studied and on the availability of a pulsed laser having the required peak power, energy per pulse, pulse duration, and beam quality. With the schemes reported in Figure 10, *all* the elements except He and Ne can be detected.[308]

The analytical implications of such technique seem, therefore, to be impressive because of the achievement of the ultimate analytical sensitivity possible. RIS, in addition to its single atom detection capability, has also applications to classical phenomena such as the diffusion of free atoms and a variety of atomic fluctuation phenomena, and to photophysics measurements such as collisional studies involving excited states and the evaluation of their photoionization cross sections.[307]

Fairbank and She[309] have compared the RIS method with the laser excited fluorescence (of both resonance and nonresonance type) technique in terms of single atom detection capabilities. The main disadvantage of the fluorescence method seems to be its limited applicability. Falk,[310] in a discussion of the theoretical sensitivity of laser spectrometric methods, has also discussed the RIS techniques pointing out that, in practical atomizers such as flames, thermal ionization might be a severe drawback for the conventional analytical applications of this method.

VII. SIGNAL-TO-NOISE RATIOS AND DETECTION LIMITS IN LASER SPECTROMETRY

A. General Comments

In this section, expressions (not derived but referenced) will be given for the signal-to-noise ratios for various types of laser spectrometry under limiting conditions which can be applied in certain cases. The detection limit in spectroscopy is defined as that concentration, C_{Lim} resulting in a S/N of 3.[311] Similar considerations, together with an evaluation of the minimum detectable concentration of atoms and molecules by several laser spectrometric methods, can be found in the papers by Falk[310] and Morgan.[312] Alkemade[313] has also discussed the various single atom detection techniques based on laser excitation.

B. Signal-to-Noise Expressions — Gas Phase

The expressions in this section will be taken from Winefordner et al.,[314] Tolles and Turner,[257] and Omenetto and Winefordner[2] for two-level atoms or molecules. In addition, expressions for the signal-to-noise ratios will be given only for the major

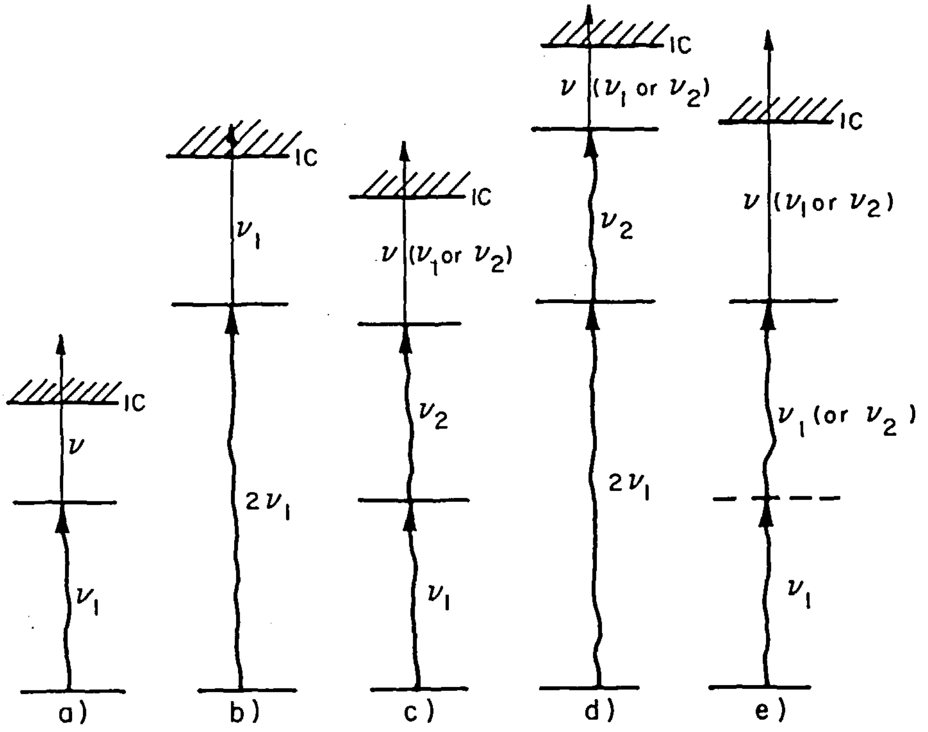

FIGURE 10. RIS detection schemes. Ionization is achieved with: (a) two photons at the same frequency ν_1; (b) one frequency doubled photon at $2\nu_1$ and one photon at ν_1; (c) two photons at frequency ν_1 or ν_2 and one photon at frequency ν_1 or ν_2; (d) one frequency doubled photon at $2\nu_1$ and two photons at ν_2 or one photon at ν_2 and one photon at ν_1; (e) one photon at frequency ν_1 or ν_2 from a state reached by a two-photon allowed transition at ν_1. (Redrawn from Hurst, G. S., Nayfeh, M. H., and Young, J. P., *Appl. Phys. Lett.*, 30, 229 (1977).)

limiting noise present in the measurements. Therefore, the detection limits in real analytical situations will be expected to be poorer than the calculated ones. Moreover, no real significance should be given to the extremely low limits calculated since the limiting noise due to the fluctuations of atoms in the probe volume[310,313] has not been considered here.

Absorption (Atomic or Molecular) Continuum Source — No Saturation — Source Shot Noise:

$$\left(\frac{S}{N}\right)_{ACS} \cong \frac{\left(\int_0^\infty \sigma(\lambda)d\lambda\right) n_o \ell_A B_{c\lambda}(\lambda_o) K_A D_S}{\sqrt{2 B_{c\lambda}(\lambda_o) \Delta\lambda_S K_A D_S}} \qquad (3)$$

Absorption (Atomic or Molecular) Line Source — No Saturation — Source Shot Noise:

$$\left(\frac{S}{N}\right)_{ALS} = \frac{\sigma_o \delta_o \, n_o \ell_A B_L K_A D_S}{\sqrt{2 B_L K_A D_S}} \qquad (4)$$

Fluorescence (Atomic or Molecular) Continuum Source — No Saturation — Detector Shot Noise:

$$\left(\frac{S}{N}\right)_{FCD} = \frac{\left(\frac{1}{4\pi}\right)\left({}_{o}\int^{\infty} \sigma(\lambda)d\lambda\right) n_o \ell_F Y B_{C\lambda}(\lambda_o) K_F D_S}{\sqrt{2R_D t_o}} \tag{5}$$

Fluorescence (Atomic or Molecular) — Continuum Source — No Saturation — Background Shot Noise:

$$\left(\frac{S}{N}\right)_{FCB} = \frac{\left(\frac{1}{4\pi}\right)\left({}_{o}\int^{\infty} \sigma(\lambda)d\lambda\right) n_o \ell_F Y B_{C\lambda}(\lambda_o) K_F D_S}{\sqrt{2B_{B\lambda}(\lambda_o)\Delta\lambda_S K_B D_B}} \tag{6}$$

Fluorescence (Atomic or Molecular) Line Source — No Saturation — Detector Shot Noise:

$$\left(\frac{S}{N}\right)_{FLD} = \frac{\left(\frac{1}{4\pi}\right)\sigma_o \delta_o n_o \ell_F B_L Y K_F D_S}{\sqrt{2R_D t_o}} \tag{7}$$

Fluorescence (Atomic or Molecular) Line Source — No Saturation — Background Shot Noise:

$$\left(\frac{S}{N}\right)_{FLB} = \frac{\left(\frac{1}{4\pi}\right)\sigma_o \delta_o n_o \ell_F B_L Y K_F D_S}{\sqrt{2B_{B\lambda}(\lambda_o)\Delta\lambda_S K_B D_B}} \tag{8}$$

Spontaneous Raman Scattering — Line Source — Detector Shot Noise:

$$\left(\frac{S}{N}\right)_{SRD} = \frac{\phi_L n_o \ell_R K_R D_S \left(\frac{d\sigma_R}{d\Omega}\right)}{\sqrt{2R_D t_o}} \tag{9}$$

Fluorescence (Atomic or Molecular) Continuum Source — Saturation — Detector Shot Noise:

$$\left(\frac{S}{N}\right)_{FCD\text{-}S} = \frac{\left(\frac{\ell_F}{4\pi}\right) n_o \left(\frac{1}{2}\right) A_{21} h\nu_o K_F' D_S \alpha_S}{\sqrt{2R_D t_o}} \tag{10}$$

Fluorescence (Atomic or Molecular) Continuum Source — Saturation — Background Shot Noise:

$$\left(\frac{S}{N}\right)_{FCB\text{-}S} = \frac{\left(\frac{\ell_F}{4\pi}\right) n_o \left(\frac{1}{2}\right) A_{21} h\nu_o K_F' D_S \alpha_S}{\sqrt{2B_{B\lambda}(\lambda_o)\Delta\lambda_s K_B D_B}} \tag{11}$$

Fluorescence (Atomic or Molecular) Line Source — Saturation — Detector Shot Noise:

$$\left(\frac{S}{N}\right)_{FLD\text{-}S} = \frac{\left(\frac{\ell_F}{4\pi}\right) n_o \left(\frac{1}{2}\right) \eta A_{21} h\nu_o K_F' D_S \alpha_S}{\sqrt{2R_D t_o}} \tag{12}$$

Fluorescence (Atomic or Molecular) Line Source — Saturation — Background Shot Noise:

$$\left(\frac{S}{N}\right)_{FLB-S} = \frac{\left(\frac{\ell_F}{4\pi}\right) n_o \left(\frac{1}{2}\right) \eta A_{21} h\nu_o K'_F D_S \alpha_S}{\sqrt{2B_{B\lambda}(\lambda_o)\Delta\lambda_S K_B D_B}} \tag{13}$$

Fluorescence (Atomic or Molecular) Line Source — Two-Photon Excitation — Detector Shot Noise:

$$\left(\frac{S}{N}\right)_{F2P-D} \cong \frac{\left(\frac{\ell_F}{4\pi}\right)\left(\frac{E_L}{h\nu_o}\right)^2 \sigma^{(2)} \eta n_O D_s K''_F}{\sqrt{2R_D t_o}} \tag{14}$$

CARS — Detector Noise Limit:

$$\left(\frac{S}{N}\right)_{CARS-D} \cong \frac{\left(\frac{4\pi^2 \omega_{as}}{c^2}\right)^2 E_p^2 \phi_S \chi^2 \ell_R^2 K'_R D_S n_s^2 \left(\frac{d\sigma_R}{d\Omega}\right)^2}{\sqrt{2R_D t_O}} \tag{15}$$

No theoretical relationships are given for optogalvanic and optoacoustic methods, since the authors do not know of suitable S/N expressions for flames. The symbols (and units) used in the above expressions are defined below:

$\int\sigma(\lambda)d\lambda$ = integrated absorption cross section for line or band, $cm^2 nm$

$= \left(\frac{\pi e^2}{mc}\right)\left(\frac{\lambda_o^2}{c}\right) f_{12}$, $cm^2 nm$

m,e = mass, charge of electron, g, esu

c = speed of light, $cm\ s^{-1}$

$\frac{\pi e^2}{mc}$ = 0.027 cm^2 Hz

λ_o = peak (central) wavelength of absorption (luminescence), cm or nm

$\frac{\lambda_o^2}{c}$ = conversion factor from Hz to nm, × 10^7 nm Hz^{-1}

f_{12} = absorption oscillator strength, dimensionless

n_o = total concentration of absorbers (analyte) in the ground state, cm^{-3}

ℓ_A = absorption path length in absorption spectrometry, cm

$B_{C\lambda}(\lambda_o)$ = spectral radiance of continuum source at λ_o, $J\ s^{-1}\ cm^{-2}\ nm^{-1}\ sr^{-1}$

K_A = optical-detector factor for absorption spectrometry, cm^2 sr s J^{-1}

$= \Omega_{ex}(wh)_{ex} T_s \eta_d t_o \left(\frac{1}{h\nu_o}\right)$; cm^2 sr s J^{-1}

Ω_{ex} = excitation solid angle, sr

$(wh)_{ex}$ = (slit width) × (slit width) of excitation spectrometer; cm^2

η_d = photodetector efficiency (counts per photon in cathode), dimensionless

T_s = overall transmission of excitation optical system dimensionless

t_o = observation (integration, measurement, counting) time, s

$h\nu_o$ = energy of absorbed (fluorescent; scattered) photon, J

D_s = measurement duty factor for signal (fractional "on" time), dimensionless

$\Delta\lambda_s$ = spectrometer bandpass, nm

σ_o = peak absorption coefficient, cm^2

$= \left(\frac{2\sqrt{\ell n 2}}{\sqrt{\pi}}\right)\left(\frac{\pi e^2}{mc}\right)\left(\frac{\lambda_o^2}{c}\right)\frac{f_{12}}{\Delta\lambda_D}$; cm^2

$\Delta\lambda_D$ = Doppler (Gaussian) half width of peak, nm

δ_σ = convolution overlap integral accounting for peak shifts and widths of line (excitation source and absorption line) or band (evaluated from Voigt integral), dimensionless

B_L = integral radiance of line source at λ_o, $J\ s^{-1}\ cm^{-2}\ sr^{-1}$

ℓ_F = fluorescence path length, cm

Y = fluorescence quantum (power) efficiency, dimensionless

K_F = optical-detector factor for fluorescence excitation and emission, $cm^2 sr^2 s\ J^{-1}$

$= \Omega_{ex}\Omega_{f}\ell(wh)_{em}T_{\sigma}\eta_{d}t_{b}\left(\frac{1}{h\nu_{\sigma}}\right)$, cm^{2}sr^{2}s J^{-1}

Ω_F = fluorescence solid angle of collection, sr

$(wh)_{em}$ = (slit width) × (slit width) of emission monochromator observing fluorescence, cm^2

T_σ = overall transmission including excitation and emission optics in fluorimetric system, dimensionless

R_d = detector dark count rate, s^{-1}

K_B = optical detector factor for background, cm^{2}sr s J^{-1}

D_B = measurement duty factor for background, dimensionless

ϕ_L = flux of line source used for Raman (spontaneous) scatter, J s^{-1}

ℓ_R = Raman interaction region, cm

K_R = optical-detector factor for Raman scatter

$= \Omega_{em}\, T_o\, \eta d\, t_o \left(\frac{1}{h\nu_\sigma}\right)$, sr s J^{-1}

$\frac{d\sigma_R}{d\Omega}$ = differential Raman cross section, cm^2 sr^{-1}

A_{21} = Einstein coefficient of spontaneous emission, s^{-1}

K_F' = optical-detector factor for saturated fluorescence, cm^2 sr s J^{-1}

α_s = beam expansion factor for laser source in fluorescence when near saturation conditions can be maintained after expansion, dimensionless

E_L = line source irradiance, J s^{-1} cm^{-2}

$\sigma^{(2)}$ = two-photon absorption cross section, cm^4 s

η = fraction of atoms or molecules excited with narrow line source, i.e., ratio of homogeneous to inhomogeneous half widths (Lorentztan to Doppler), dimensionless

K_F'' = optical detector factor for two-photon fluorescence, cm^2 sr s

ω_{as} = $2\pi\nu_{as}$ = angular anti-Stokes Raman scatter frequency, Hz

E_p = irradiance of CARS pump beam, J s^{-1} cm^{-2}

ϕ_s = flux of CARS Stokes beam, J s^{-1}

χ' = modified susceptibility for resonant conditions, cm^4 sr J^{-1}

χ = susceptibility = $\chi' \frac{d\sigma_R}{d\Omega} n_o$, cm^3 J^{-1}

K_R' = $T_o\eta_d t_o\left(\frac{1}{h\nu_o}\right)$, s J^{-1}

Several comments should be made about the above expressions:

1. It is assumed that the continuum source cases involve a flat source spectral distribution over the line or band in all cases.
2. It is assumed that the line source cases involve a source line considerably narrower than the absorption line or band.
3. It is assumed that the optical detector system responds in a constant manner at all measurement wavelengths.
4. It is assumed that the absorbance is low in all cases.
5. It is assumed that only *one* noise source is present for each case.
6. It is assumed that the source does not cause any reactions, temperature change, and coherency effects upon passing through the sample.
7. For the cases of molecular fluorescence, it is assumed that the fluorescence over all wavelengths is measured.
8. For the case of a condensed phase medium, the above expressions still hold except different noises may become apparent, e.g., source transmission flicker noise in absorption spectrometry and impurity fluorescence shot and flicker noises in fluorescence spectrometry.

C. Estimation of Minimum Detectable Concentration of Analytes by Absorption, Fluorescence, and Raman Scatter Methods[2,112,246,247,257,310]

Using the above expressions for S/N for each of the various methods, $n_o)_{lim}$ values,

Table 9
CALCULATED LIMITS OF DETECTION[a] IN SPECIES/CM^3 FOR ANALYTE SPECIES MEASURED BY SEVERAL METHODS

	Limit of Detection (cm^{-3}), wavelength of transition			
	300 nm, Sample temperature		**600 nm, Sample temperature**	
Method-source-key	**300 K**	**2500 K**	**300 K**	**2500 K**
Absorption-continuum (ACS)	3×10^7	3×10^7	6×10^7	6×10^7
Absorption-line (ALS)	2×10^4	4×10^4	5×10^3	2×10^4
Fluorescence-continuum (FCD)	1×10^3	1×10^3	2×10^2	2×10^2
Fluorescence-continuum (FCB)	6×10^6	6×10^6	2×10^5	2×10^5
Fluorescence-line (FLD)	7×10^2	2×10^3	2×10^2	5×10^2
Fluorescence-line (FLB)	4×10^6	1×10^7	2×10^5	5×10^5
Raman (SRD)	1×10^{14}	1×10^{14}	2×10^{17}	2×10^{17}
Fluorescence-continuum (FCD-S)	3×10^0	3×10^0	3×10^0	3×10^0
Fluorescence-continuum (FCB-S)	2×10^1	2×10^1	3×10^0	3×10^0
Fluorescence-line (FLD-S)	3×10^2	3×10^2	3×10^1	3×10^2
Fluorescence-line (FLB-S)	2×10^3	2×10^3	3×10^2	3×10^2
Fluorescence-line (F2P-D)	7×10^8	7×10^8	2×10^7	2×10^7
Coherent AS Raman (CARS-D)	5×10^{15}	5×10^{15}	5×10^{10}	5×10^{10}

Note: See text for expressions used and evaluation of parameters. The analyte is any hypothetical species with characteristics listed in text. Values given are "order of magnitude" estimates.

[a] Limit of detection is that concentration of species, n_0, resulting in a S/N = 3.

i.e., the limit of detection in species per cm^3, can be estimated; these values appear in Table 9. The choice of parameters used to estimate the $n_o)_{lim}$ values are discussed below

Absorption values — ($f_{12} = 1$, $\lambda_o = 300$ nm or 600 nm)

- $\int \sigma(\lambda) d\lambda = 8.1 \times 10^{-15}$ cm^{2}nm at 300 nm
  $= 3.2 \times 10^{-14}$ cm^{2}nm at 600 nm
- $\sigma_o = \dfrac{8.1 \times 10^{-15}}{\Delta\lambda_D}$ cm^{2}nm^{-1} at 600 nm
  $= \dfrac{3.2 \times 10^{-14}}{\Delta\lambda_D}$ cm^{2}nm^{-1} at 600 nm
- $h\nu_o = 6.6 \times 10^{-19}$ J at 300 nm
  $= 3.3 \times 10^{-19}$ J at 600 nm
- $\Delta\lambda_D = 7.16 \times 10^{-7} \lambda_o \dfrac{\sqrt{T}}{M}$ (assume analyte has M = 50 amu)
  $= 1.5 \times 10^{-3}$ nm at 300 nm and T = 2500 K
  $= 5.4 \times 10^{-4}$ nm at 300 nm and T = 300 K
  $= 3.1 \times 10^{-3}$ nm at 600 nm and T = 2500 K
  $= 1.1 \times 10^{-3}$ nm at 600 nm and T = 300 K
- $\delta_o \simeq 1.0$ (for a narrow line source/absorber system)
- $B_{C\lambda}$ (λ_o = 300 nm or 600 nm) = 10^{-1} J s^{-1}cm^{-2}sr^{-1}nm^{-1} (for a xenon arc lamp) (also $D_s = 0.5$)

- B_L (λ_o = 300 nm or 600 nm) = 10^{-4} J $s^{-1}cm^{-2}sr^{-1}$ (for a good electrodeless discharge) (also $D_2 = 0.5$)
- $\Delta\lambda_s$ = 1 nm (for spectrometer)
- ℓ_A = 10 cm
- $K_A = \Omega_{ex}(wh)_{ex} T_s \eta_d t_o \left(\frac{1}{h\nu_o}\right) cm^2 sr\ s\ J^{-1}$

  $= 0.02\ sr \times 0.05\ cm \times 1\ cm \times 0.5 \times 0.5 \times 10\ s \times \frac{1}{h\nu_o}$

  $= 2.5 \times 10^{-3} \left(\frac{1}{h\nu_o}\right) cm^2 sr\ s\ J^{-1}$
- t_o = 10 s

Fluorescence values — ($f_{12} = 1$, λ_o = 300 nm or 600 nm) — No Saturation

- $\int\sigma(\lambda)d\lambda$, σ_o, $h\nu_o$, δ_o, $B_{C\lambda}$, $\Delta\lambda_s$, $\Delta\lambda_D$, and B_L are assumed to be the same as for absorption measurements
- Y = 0.02 for C_2H_2/air flame (T = 2500 K)

  = 0.02 for gas cell (T = 300 K, 1 atm)
- ℓ_F = 1 cm
- $B_{B\lambda}$ (λ_o = 300 nm) = 10^{-6} J $s^{-1}cm^{-2}sr^{-1}nm^{-1}$ (C_2H_2/air flame)
- $B_{B\lambda}$ (λ_o = 600 nm) = 10^{-8} J $s^{-1}cm^{-2}sr^{-1}nm^{-1}$ (C_2H_2/air flame)
- $B_{B\lambda}$ (λ_o = 300 nm or 600 nm) $\cong$ 0 (T = 300 K)
- D_B = 1 for all conventional fluorescence measurements
- $R_D = 10^3\ s^{-1}$ (for a *good* photomultiplier detector)
- $K_F = \Omega_{ex}\Omega_{f\ell}(wh)_{em} T_\sigma \eta_d t_o \left(\frac{1}{h\nu_o}\right) = 1\ sr \times 1\ sr \times 0.1\ cm \times 1\ cm \times 0.5 \times 0.5 \times 10s \times \frac{1}{h\nu_o}$

  $= 2.5 \times 10^{-1} \left(\frac{1}{h\nu_o}\right) cm^2 sr^2 s\ J^{-1}$
- t_o = 10 s

Fluorescence values — ($A_{21} = 10^8\ s^{-1}$, λ_o = 300 nm or 600 nm) — Saturation

$h\nu_o$, $B_{B\lambda}$ (λ_o = 300 nm or 600 nm), R_D, t_o, $\Delta\lambda_s$, and K_F are assumed to be the same as for fluorescence — no saturation cases. The "continuum" (pseudo) and narrow line lasers assumed for this case have spectral radiances and irradiances, respectively, exceeding the saturation spectral radiances and irradiances for the atoms or molecules absorbing at λ_o = 300 nm and at λ_o = 600 nm. Also, $D_2 = 10^{-6}$; $D_B = 10^{-6}$ (for pulsed N_2-pumped dye laser and gated detector); $\alpha_s = 10^2$ (100-fold expansion in the above laser beam while still maintaining near saturation conditions); $\eta = 10^{-2}$ (assuming the ratio of laser line width to Doppler width is $\approx 10^{-2}$). (The choice of $A_{21} = 10^8\ s^{-1}$ is for convenience; it should be stressed that an $f_{12} = 1$ and λ_o = 300 nm or 600 nm transposes to an $A_{21} > 10^8\ s^{-1}$ in both cases.)

Raman (spontaneous) values

- $\frac{d\sigma_R}{d\Omega} = 10^{-30}\ cm^2 sr^{-1}$ (at λ_o = 600 nm)

$= 10^{-27}\ \mathrm{cm^2 sr^{-1}}$ (at $\lambda_o = 300$ nm; near resonance enhancement)

- $\ell_R = 1$ cm
- $K_R = \Omega_{em}\, T_o \eta_d t_o \left(\frac{1}{h\nu_o}\right) = 0.02\ \mathrm{sr} \times$

  $0.5 \times 0.5 \times 10\ \mathrm{s} \times \frac{1}{h\nu_o}$

  $= 5 \times 10^{-2} \left(\frac{1}{h\nu_o}\right)\ \mathrm{sr\ s\ J^{-1}}$

Two-photon fluorescence values

- $\sigma^{(2)} = 10^{-51}\ \mathrm{cm^2/photon/cm^2\ s}$
- $\eta = 10^{-2}$ (same as for fluorescence — saturation)
- E_L ($\lambda_o = 300$ nm) $= 10^9\ \mathrm{J\ s^{-1}\ cm^{-2}}$ (pulsed flashlamp dye laser doubled)
- E_L ($\lambda_o = 600$ nm) $= 10^{10}\ \mathrm{J\ s^{-1}\ cm^{-2}}$ (pulsed flashlamp dye laser)
- $D_s = 10^{-6}$
- $K_F = 2.5 \times 10^{-1} \left(\frac{1}{h\nu_o}\right)$ (same as for fluorescence)
- $R_D = 10^3\ \mathrm{s^{-1}}$
- $t_o = 10$ s

CARS values — (Assume Nd-YAG doubled, $\lambda_p = 532$ nm, $\lambda_s = 607$ nm, $\lambda_{as} = 473$ nm.)

- $\omega_{as} = 2\pi\, \nu_{as} = 4.0 \times 10^{15}$ Hz
- $E_p = 5 \times 10^9\ \mathrm{J\ s^{-1} cm^{-1}}$ (at $\lambda_p = 532$ nm)
- $\phi_s = 10^5\ \mathrm{J\ s^{-1}}$ (at $\lambda_s = 607$ nm)
- $D_s = 10^{-6}$
- $R_D = 10^3\ \mathrm{s^{-1}}$
- $t_o = 10$ s
- $\frac{d\sigma_R}{d\Omega} = 10^{-30}\ \mathrm{cm^2 sr^{-1}}$ (for vibrational Q of N_2)
- $\chi' = 3 \times 10^2\ \mathrm{cm^4 sr\ J^{-1}}$
- $\ell_R = 1$ cm

D. Discussion of Calculated Limits of Detection

It is apparent from the results of Table 9 that such values are rarely achieved or even approached in experimental absorption, fluorescence, and Raman spectrometry. The reasons for this are intimately related to several assumptions and choices of parameters for estimating the limits of detection. For example, we assumed initially that only shot noise was important, and furthermore, for each case, only one limiting type of shot noise was significant. In reality, more than one source of shot noise may be important, but even more important, various flicker noises may appear. In addition, the instrumental factors like K_A, K_F, K_R, and the source intensities were estimated for ideal experimental conditions, and even though better values are achievable in practice, the chosen values may be too liberal. Finally, the transition probabilities (f_{12} and A_{21}) were chosen for a very intense atomic or molecular transition.

Some simple, obvious, but worthwhile conclusions from the limits of detection in Table 9 and the signal-to-noise ratio expressions are given below:

1. For absorption, fluorescence (no saturation), fluorescence (saturation), and

fluorescence (two photon), the detection limit will increase (become poorer) by 10 times if: (a) the transition probability, f_{12} or A_{21}, decreases by 10 times; and (b) the fluorescence path length is decreased by 10 times.

2. For absorption, fluorescence (no saturation) — background noise limited and fluorescence (saturation) — background noise limited, the detection limit will increase (become poorer) by 10 times if: (a) the background spectral radiance (for fluorescence, the background is from the cell; for absorption, the background is from the source itself) increases by 100 times; (b) the spectral bandwidth (for continuum background only) of the spectrometer increases by 100 times; (c) the instrumental factor K_A or K_F decreases by 100 times; and (d) the signal duty factor decreases by 10 times; (assuming the background duty factor remains the same); if the signal and background duty factors are interrelated as with a boxcar detector, then they must decrease by 100 times.
3. For fluorescence (saturation), the limits of detection do *not* vary with source intensity unless the source intensity change (decrease) results in a need to reduce the beam expansion factor to maintain near saturation conditions; if the source power can be maintained for a longer pulse width, then D_S (and D_B) can be increased, resulting in a corresponding decrease in the detection for the detector noise limit and in a square root decrease in the detection for the background noise limit; thus higher power, longer pulse width lasers (which also cost more) are nice for analysis since the beam expansion factor can be increased as well as the duty factors.
4. For spontaneous Raman scatter and detector noise limitation, the detection limit will increase (become poorer) by 10 times if: (a) the source flux is reduced by 10 times; (b) the interaction length is reduced by 10 times; (c) the differential cross section is reduced by 10 times; (d) either the instrumental factor or duty factor are reduced by 10 times; (e) the dark count rate is increased by 100 times; and (f) the observation time is reduced by 100 times.
5. For CARS and detector noise limitation, the detection limit will be increased by 10 times if: (a) the interaction region is $\sqrt{10}$ times smaller; (b) the susceptibility is $\sqrt{10}$ times smaller; (c) the probe laser irradiance is $\sqrt{10}$ times smaller; (d) the Stokes laser flux is 10 times smaller; (e) the differential cross section is $\sqrt{10}$ times smaller; (f) the dark count rate and/or observation time are 10^2 times larger and/or smaller, respectively; and (g) the instrumental factor, K_R' is 10 times smaller.
6. For molecular fluorescence (two-photon excitation), the detector noise limit is reduced by 10 times if: (a) the source intensity is decreased by $\sqrt{10}$ times; (b) the absorption cross section is reduced by 10 times; (c) the duty factor, D_s, is reduced by 10 times; (d) the instrumental factor, K_F, is reduced by 10 times; and (e) the dark count rate is increased by 100 times or the observation time is reduced by 100 times.

In Table 9, calculated detection limits in terms of species per cm^3 are listed. In the previous section, some of the reasons were given why the calculated and experimental values might differ in terms of (molecules or atoms) per cm^3. However, no mention was given of the inefficient conversion of sample species to measured species. In *condensed phase* molecular spectrometry, the conversion from analyte concentration, C, in moles per liter, to n_O in molecules per cm^3, is simply given by

$$n_o = 10^{-3}\beta_m \cdot C \cdot N_A \qquad (16)$$

where N_A is Avogadro's number (6×10^{23}) and β_m is the fraction of analyte species present in the correct form for the spectroscopic transition, e.g., β_m will depend upon pH, temperature, complexing species, etc. In *static gas phase* atomic or molecular spectrometry where the sample is vaporized by a thermal process (assuming solid or liquid material exists in the cell),

$$n_o = \frac{\beta_m \rho_s}{kT} \tag{17}$$

where ρ_s is the saturation vapor pressure, torr, k is the Boltzmann constant (torr $K^{-1}cm^3$), and T is the temperature (in K) of the cell. In *dynamic gas phase* atomic or molecular spectrometry where the sample solution is converted to submicroscopic species via an aerosol intermediate, as in flame spectrometry,

$$n_o = \frac{\beta_m(\text{or } \beta_a)\epsilon\beta_v FCN_A \cdot 10^{-3}}{Qe_f} \tag{18}$$

where β_v is the vaporization fraction, β_m (or β_a) is the fraction of analyte species present in the measured gaseous system as molecules or as atoms, ϵ is the fraction of solution sprayed into a chamber which is transferred as aerosol into the hot gases, F is the sample solution transport rate (cm^3s^{-1}), C is the analyte concentration (mol ℓ^{-1}), N_A is Avogadro's number, Q is the flow rate of gases at room temperature (in cm^3s^{-1}), and e_f is the gas expansion factor due to heating of the gases from room temperature to some hot gas temperatures. For a furnace system[315] where the sample is instantaneously vaporized into a cell volume, V_c, cm^3,

$$n_o = \frac{\beta_m(\text{or } \beta_a)\beta_v wN_A}{M_a V_c} \tag{19}$$

where β_m or β_a are as above, β_v is the fraction of species introduced which appear finally in the gas phase, i.e., accounts for losses due to carbide formation, particles condensing out in the ends of the furnace, etc., w is the weight, in g, of the sample introduced, M_a is the molecular (atomic) weight of the pure material, and N_A is Avogadro's number. It is assumed in the latter case that the atomization times, t_a, are much less than the residence time, t_r, of species in the cell where $t_r = L^2/8D$, where L is the length of the furnace, and D is the analyte diffusion coefficient at the furnace temperature.

In any event, it should be pointed out that the β factors account for losses of the analyte. In condensed phase work, the β value will often be unity indicating no losses. For static gas phase work, there will also be few gas phase losses in many cases. However, in such studies, there is the obvious "loss" in going from a small amount of analyte in the solid or liquid phase to a larger volume in the gas phase. In flames, plasmas, etc., there are not only the losses due to the above named β-factors but also those due to conversion of a volume of liquid sample to a gas. For example, 1 mmol of analyte is converted to 22.4 mℓ of gas (assuming an ideal gas) at 273.1 K (~ 10 times or 224 mℓ of gas at 2500 K) and is further diluted by a rapidly flowing stream of hot gas which supplies the flame. For furnaces, the latter dilution is insignificant since the system is static, but the "loss' due to conversion of the analyte from the solid or liquid phase to the gas phase is important; finally, complex losses of analyte in furnaces can occur through either vaporization losses prior to the measurement, as $AsCl_3$, or *in situ* losses of analyte by forming carbides, such as ZrC_2.

It may be instructive to give the conversion factor from moles per liter to atoms per cm^3 of flame gases for a typical atomic flame spectrometric measurement. Assume an analysis is to be performed on an element Z which is present at concentration, moles per ℓ, in solution and is introduced into a flame at a liquid flow rate of 0.2 cm^3/s. Assume the nebulizer efficiency ϵ is 0.02, the efficiency of conversion of droplets to submicroscopic species, $\beta_v = 0.5$, and a total gas flow rate, Q of 200 cm^3/s with a flame temperature of ~2500 K ($e_f \sim 10$). This system could represent a typical C_2H_2/air flame with nebulizer burner such as is used in atomic absorption flame spectrometry. Then

$$\frac{n_o}{C} = 6 \times 10^{14} \times \beta_a \qquad (20)$$

Therefore, if element $Z(M_a = 100$ amu) has a concentration of 10^{-9} *M* (10^{-4} μg/mℓ or 0.1 ppb), then $n_o = 6 \times 10^5$ atomic species per cm^3, which is typical of detection limits in atomic fluorescence flame spectrometry, if the atomization efficiency (β_a) is unity.

No attempt will be made here to correlate experimental detection limits with theoretical ones, not only because of lack of space, but more importantly, lack of adequate physical parameters to evaluate the S/N ratio expressions for specific experimental systems.

E. Analytical Figures of Merit (Experimental)

In Table 10 and 11, approximate limits of detection (LOD), linear dynamic ranges (LDR), precisions (% RSD — % relative standard deviations), and minimum sample sizes for the various laser methods are listed. Also several other methods are listed for comparison purposes.

F. Experimental Limits of Detection

In Tables 2 to 5, experimental limits of detection for atoms (Tables 2 and 3) and for molecules (Tables 4 and 5) are given. The molecular detection limits are further divided according to gas phase (Table 5) and condensed phase (Table 4), and in the condensed phase according to the technique fluorimetry (Table 4) and phosphorimetry (Table 6). The gas phase atomic-spectrometric detection limits are given not only for laser excited atomic fluorescence, but also for conventional line-source excited atomic fluorescence, conventional continuum-source excited atomic fluorescence, conventional line-source atomic absorption flame spectrometry, and for atomic emission spectrometry with an inductively coupled plasma. No tables for absolute detection limits will be given for molecules because estimates can be made from the data in the tables by multiplying the concentrational detection limit by the cell volume or interaction volume; in other words, the systems used to detect small amounts of molecules are identical to those used to detect small concentrations of molecules. However, in the case of elemental analysis, furnace methods are used in atomic absorption and atomic fluorescence rather than flames, plasmas, etc., which are used for concentration measurements. Therefore, in Table 3, examples of elemental detection limits for atomic fluorescence, atomic absorption furnace, and atomic emission with the inductively coupled plasma methods are given.

It is apparent that laser methods are extremely sensitive methods capable of excellent precision, long linear dynamic ranges, and microsampling (also see Tables 10, 11). Certainly Arthur Robinson's[6] catchy title in *Science,* "Analytical Chemistry: Using Lasers to Detect Less and Less", is valid and the detection of even less is to be expected. The considerable advances since Steinfeld's excellent review[1] are also important.

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Table 10
DETECTION LIMITS (LOD), LINEAR DYNAMIC RANGES (LDR), AND PRECISION (%RSD) OF MOLECULES (pg) BY SEVERAL LASER SPECTROMETRIC METHODS

Method	Practical LOD (pg)	%RSD	LDR	Estimated LOD[a] (pg)	Ref.
Laser fluorimetry	1	1—2	$\approx 10^5$	10^{-3}	160
Xenon fluorimetry	1	1—2	$\approx 10^5$	1	[b]
Laser phosphorimetry	10^3	1—5	$\approx 10^4$	1	214
Laser fluorescence microscopy (tagging of molecule)	10^{-1}	2	?	$10^{-10} 10^{-13}$	[c]
Laser Raman (spontaneous)	$\approx 10^6$	2—5	$\approx 10^3$	$\approx 10^5$	220
Laser Raman (resonance)	$\approx 10^4$	2—5	$\approx 10^3$	$\approx 10^2$	227, 228
Laser Raman (CARS)	$\approx 10^5$	5—10	$\approx 10^2$	$\approx 10^4$	220
Laser Raman (inverse)	$\approx 10^5$	2—5	$\approx 10^3$	$\approx 10^3$	243
Laser-thermal lensing	$\approx 10^5$	1—5	≈ 10	$\approx 10^3$	108,109
Laser Raman microprobe	≈ 1	?	?	$\approx 10^{-1}$	264

[a] Best estimate based on detector noise limit.

[b] Guilbault, G. G., *Practical Fluorescence, Theory, Methods, and Techniques*, Marcel Dekker, New York, 1973.

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Table 11
DETECTION LIMITS (LOD), LINEAR DYNAMIC RANGES (LDR), AND PRECISION (%RSD) OF ELEMENTS (pg) BY SEVERAL LASER SPECTROMETRIC METHODS

Method	Sample size[a]	Practical LOD (pg)	%RSD	LDR	Estimated LOD[b] (pg)
Laser exc AFS[c]	0.1—1	10^2–1	1—2	10^5—10^6	10^{-5}—10^{-2}
Conventional EDL AFS[c]	0.1—1	10^1	1—2	10^4—10^5	1
Conventional xenon AFS[c]	0.1—1	10^3	1—2	10^3—10^4	10^2
Laser Exc optogalvanic[c]	0.1—1	10^2–1	1—5	10^5—10^6	10^{-3}
Laser emission microprobe[d]	10^{-8} (10—200 μm)[e]	10^{-3}–1	5—15	10^2—10^3	10^{-5}—10^{-2}
Laser mass spectrometer[f]	10^{-10}—10^{-12} (1 μm)[e]	10^{-6}—10^{-8}	$\approx$5—10	$\approx 10^3 10^3$—10^4	10^{-7}—10^{-9}
Laser atomization AA[g]		10^1—10^2	$\approx$5—15	$\approx 10^2 10^1$—10^2	1—20
Ion microprobe	10^{-11} (1—5 μm)[e]	10^{-5}—10^{-7}	$\approx$25—50	10^3—10^4	10^{-7}—10^{-9}
Neutron activation	10^{-3}—1	10^{-1}—10^2	$\approx$5—10	10^3—10^4	10^{-1}—10^2

[a] Minimum sample size for analysis, cm^3.

[b] The estimates are made on the basis of the author's estimates assuming detector limited noise.

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