

Laser Spectroscopy of Ultra-trace Quantities*

By C. Grey Morgan

DEPARTMENT OF PHYSICS, UNIVERSITY COLLEGE OF SWANSEA,
SINGLETON PARK, SWANSEA, SA2 8PP

1 Introduction

The invention of the laser and its rapid development during the last two decades has provided chemists with many new and powerful techniques for the synthesis of materials, novel methods for initiating chemical reactions, and for their rapid temporal or compositional analyses. Indeed, the analyst's ultimate goal, namely the ability to detect the presence of a single atom against an overwhelmingly greater concentration of different species, now lies within his grasp. To a large extent these remarkable advances have been brought about by the availability of tunable lasers which produce relatively powerful beams of coherent radiation of finely adjustable wavelengths with high temporal stability. With these it becomes possible to 'tune-in' to selected quantum states of atoms and molecules and so, by resonance absorption of laser photons, to initiate a whole variety of reactions which are otherwise difficult if not impossible to achieve. Progress in laser technology has gone hand-in-hand with improvements in radiation detection and the development of novel optical data collection and processing techniques. It is this combination which has been responsible for the extraordinary advances made in photo-chemistry and chemical spectroscopy in recent years.

Such lasers as the spin-flip Raman¹⁻³ and semiconductor diode systems^{4,5} operating in the relatively long-wavelength infrared region of the electromagnetic spectrum, dye lasers,⁶⁻⁸ generating coherent light spanning the infrared to ultra-violet portions of the spectrum, and the rapidly developing excimer and exciplex

*Based on the Introductory Lecture delivered to the Analytical Division at the Chemical Society Autumn Meeting at the University of Warwick on 20th September 1978.

¹ C. K. N. Patel and E. D. Shaw, *Phys. Rev. Letters*, 1970, **24**, 451.

² A. Mooradian, S. R. J. Brueck, and F. A. Blum, *Appl. Phys. Letters*, 1970, **17**, 481.

³ S. D. Smith, C. R. Pidgeon, R. A. Wood, A. McNeish, and N. Brignall in 'Proceedings of Laser Spectroscopy Conferences', ed. R. G. Brewer and A. Mooradian, Plenum Press, New York, 1974, p. 523.

⁴ Tunable Semiconductor lasers are reviewed by I. Melngailis and A. Mooradian in 'Laser Applications to Optics and Spectroscopy', ed. S. Jacobs, M. Sargent, M. Scully, and J. Scott. Addison Wesley, 1975.

⁵ A. Mooradian, in 'Proceedings of the Sixteenth Scottish Universities Summer School, 1975', 'Nonlinear Optics', ed. P. G. Harper and B. S. Wherett, Academic Press, 1977.

⁶ J. K. Burdett and M. Poliakoff, *Chem. Soc. Rev.*, 1974, **3**, 293.

⁷ S. A. Tuccio, K. H. Drexhage, and G. A. Reynolds, *Optics Comm.*, 1973, **7**, 243.

⁸ D. J. Bradley, *Opt. Electronics*, 1974, **6**, 25.

lasers⁹⁻¹² generating quite short-wavelength ultraviolet light are revolutionising spectroscopy. The extraordinary spectral purity of laser light, the large intensities or photon fluxes, and the possibility of using mode-locking techniques to generate flashes of light lasting only a picosecond (10^{-12} s) make lasers the most useful and versatile type of lamp available to analysts. It is not only the analysts who benefit. For example, tunable lasers allow selective excitation and ionization of an isotope by resonance absorption of finely 'tuned-in' laser quanta. In the former process the atom or molecule is more reactive than when in its ground state and can undergo selective reactions with other chemicals and thus be removed. In the latter process the electron-ion pair are separated by an electric field and the required ion species collected. The small nuclear mass differences between isotopic components of an atomic species give different electron energy levels and ionization potentials, so, by carefully tuning into resonance, one isotope can be selectively ionized and collected. These and other laser-induced reactions are the basis of isotope separation¹³ and enrichment which is currently flourishing on a laboratory scale. It has been used to achieve enrichment of both heavy and light atoms and of molecular species and may ultimately be useful on a commercial scale for the separation of, for example, the uranium isotopes.¹⁴ Single photo-absorption of the energetic u.v. radiation from an excimer laser can also be used for isotope separation in some cases.¹⁵ Thus the 6.43 eV photon from an untuned argon fluoride excimer laser can break many chemical bonds and has in fact been used to enrich the ¹³C content of CS₂. This is possible since the ¹²CS₂ absorption spectrum lies within reach of the 6.43 eV photon but the ¹³CS₂ spectrum lies outside the range.

The separation of impurities from a gas by selective photolysis in a gas using exciplex laser radiation has recently been reported.¹⁶ The impurities in very small quantities are of importance in semiconductor manufacture. Using an argon fluoride exciplex laser, PH₃, AsH₃, and B₂H₆ impurities have been separated from SiH₄ (silane) by inducing reactions only in these impurities. The photon flux per unit mass of the impurity-contaminated silane is considerably less than if reactions also occurred with the silane and the quantum yields, *i.e.* molecules of PH₃, AsH₃, and B₂H₆ removed per photon were, respectively, 0.35, 0.42, and 0.15, permitting the production of purer silane than by other means. These impurities are the ones responsible for reduction in performance of solar cell and silicon chip devices made from silane.

⁹ D. J. Bradley, D. R. Hull, M. H. R. Hutchinson, and M. W. McGeoch, *Optics Com.*, 1945, 14, 1.

¹⁰ M. H. R. Hutchinson in 'High Power Gas Lasers', ed. E. R. Pike, Conference Series No. 29, Institute of Physics, London, 1976.

¹¹ D. J. Bradley, M. H. R. Hutchinson, and C. C. Ling, in 'Proceedings of the Leon Conference (Norway)', ed. A. Mooradian, T. Jaeger, and P. Stokseth, Springer Verlag, Berlin, 1976.

¹² J. M. Green, *Optics and Laser Technol.*, 1978, 10, 289.

¹³ V. S. Letokhov and C. Bradley Moore, 'Chemical and Biochemical Applications of Lasers', Academic Press, New York, 1977, Vol. III, present a thorough review of laser-based isotope separation processes.

¹⁴ A. S. Krass, *Science*, 1977, 196, 721.

¹⁵ T. R. Loree, J. H. Clark, K. B. Butterfield, J. C. Lyman, and R. Engleman, 'Proceedings of the Conference on Laser Interaction', 1978.

¹⁶ J. H. Clark and R. G. Anderson, *Appl. Phys. Letters*, 1978, 32, 46.

2 Laser Characteristics

It is worthwhile briefly noting here some of the temporal and spectral characteristics of laser beams. Essentially a laser comprises an active medium which may be solid, liquid, or gaseous, placed between two mirrors of reflectivities R_1 and R_2 set facing each other a distance L apart. This arrangement is called the laser cavity. The value of either R_1 or R_2 is less than unity to allow the beam of coherent radiation to form the output from the laser. Energy may be supplied to the medium in a number of ways—electrically in the case of gas and semiconductor lasers, optically, from a flash-lamp or another laser, in the case of solid-state and liquid lasers or by chemical reactions alone in the latter. Part of this energy is used to invert the normal (Maxwell-Boltzmann) distribution of excited atomic or molecular states so that the population of a particular excited level exceeds that of a lower energy level. In this inverted condition the process of stimulated emission of radiation from the excited level greatly exceeds the spontaneous emission and the coherent resonant radiation so formed is amplified by the medium. Multiple reflections along the optic axis caused by the mirrors build up a beam of coherent light for as long as energy is supplied to sustain the inversion. A certain minimum energy supply is needed for this purpose and to overcome the loss of photons extracted from the cavity in the laser beam and losses by absorption in unproductive levels in the mirrors and medium. There is thus a threshold energy requirement and minimum inversion population for the onset of laser action. As long as these are exceeded the beam will persist. This is continuous or CW operation of the laser.

If the inversion is provided only momentarily then the coherent radiation will be discharged from the cavity in a time $t_c \sim 2L/\{c(1 - R_1R_2)\}$. This time, called the cavity or photon lifetime, is typically a few hundred nanoseconds, say $\gtrsim 10^{-7}$ s, (c is the velocity of light). So in the case when the energy causing inversion is sustained only briefly—say by a millisecond flash from a pumping lamp the coherent output takes the form of a sequence of irregular flashes as stimulated emission depletes the inversion and then builds up again above threshold, to be depleted again by a flash, and so on until the energy supply fails to achieve the threshold requirement. This is called 'spiking' or 'free-running'; each flash has a duration $\sim t_c$ and is separated from the subsequent one in the sequence by the inversion build-up time, \sim tens of microseconds. Instantaneous peak powers of less than or about equal to megawatts are attained in each flash in this way in solid-state lasers such as ruby. The spiking output continues typically for about a millisecond in such pulsed lasers.

If stimulated emission and amplification are deliberately suppressed by, for example, misaligning the mirrors to prevent reflection along the optic axis or inserting an absorber or suitable shutter in the cavity in order to reduce the quality factor Q of the cavity, then a very large population inversion, vastly exceeding the threshold value, is attained. Thus there is a considerable amount of energy stored in the excited state. Sudden restoration of the Q by rapid mirror realignment, or bleaching the absorber or electronically opening the shutter releases this energy in the time t_c resulting in a single giant flash of coherent light.

This is known as Q-switching and yields peak powers of tens or hundreds of megawatts in flashes lasting about 50–100 ns in the case of neodymium-in-glass and ruby lasers.

In principle, electromagnetic waves of any wavelength λ_n can oscillate between the mirrors provided the condition $\lambda_n = 2L/n$, with $n = 1, 2, 3$ etc. is satisfied. The corresponding allowed radiation frequencies are given by $\nu_n = nc/2L$. The $e-m$ waves at these oscillation frequencies are variously called longitudinal, axial, or temporal modes. Of course only those modes which lie within the natural spectral bandwidth $\Delta\nu_{\text{amp}}$ of the active medium can oscillate and be amplified to give coherent light, so that only a restricted number of frequencies are actually observed and these lie between about 10^{13} and 10^{15} Hz. The frequency separation between adjacent modes is $\Delta\nu = c/2L$ (typically ~ 150 MHz) so that the number of simultaneously oscillating modes m is given by $m\Delta\nu = \Delta\nu_{\text{amp}}$ so $m = 2L\Delta\nu_{\text{amp}}/c$. The value of m can be quite large ($\sim 10^4$ – 10^5) since $\Delta\nu_{\text{amp}}$ can be large, e.g. $\sim 10^{12}$ Hz for neodymium-in-glass. These various modes normally oscillate independently of each other. There is no particular temporal, *i.e.* phase, relationship between adjacent modes, nor is there any special relationship between the intensities at different frequencies. They arise spontaneously from noise in the cavity and are amplified without ordered coupling. The laser output, when operating in this multimode fashion, is thus subject to rapid temporal fluctuations of intensity as the various modes interact fortuitously to combine momentarily. However, if the modes or phases can be temporally related, *i.e.* locked together in a fixed relation, the output becomes a train of flashes each of duration $2L/mc$ separated by regular intervals $2L/c$ (which is twice the cavity transit time for a photon). Thus instead of random fluctuations in the output it is transformed into a single flash of very brief duration (\sim picoseconds) repeated regularly at intervals (\sim nanoseconds) for as long as the active medium is sustained in the inverted population condition. The energy is thus concentrated repeatedly in very brief intervals of time and enormous peak powers can be achieved [\geq gigawatts (10^9 W)] by mode-locking even though the energy involved is quite small—millijoules or less. Techniques have been developed to select a single picosecond pulse from the train of mode-locked pulses. With such short durations it is possible effectively to freeze out rotational motions in molecules and hence focus on the dynamics of rotational and vibrational relaxation processes of molecules in liquids and one can then explore several related phenomena such as fluorescence depolarization, electron localization, and optical Kerr rotation in polar liquids.

Approximate characteristics of some lasers relevant to photochemistry and spectroscopy are given in Table 1. This is by no means exhaustive and is rapidly being overtaken by developments.

3 Detection of Microparticles

The relatively large light intensities from lasers make them very useful for the detection and sizing of small particulate matter by examination of the light scattered by the particles. In this way local flow velocities, particle size distribu-

Table 1

<i>Laser type</i>	<i>Wavelength /nm</i>	<i>Photon Energy /eV</i>	<i>Operational Mode</i>	<i>Power</i>
CO ₂ —low pressure	1.06×10^4	0.117	CW	watts to ~ 100 kW
CO ₂ —TEA High pressure	1.06×10^4	0.117	pulsed ($\lesssim 100$ ns)	MW
Tunable Spin- flip Raman In—Sb pumped by CO ₂ TEA laser	$\sim 9\text{—}14 \times 10^3$	$\sim 0.137\text{—}0.09$	pulsed (~ 100 ns)	$\lesssim 1$ kW
Tunable Spin- flip Raman In—Sb pumped by CO laser	$\sim 5\text{—}6 \times 10^3$	$\sim 0.248\text{—}0.21$	CW	~ 1 watt
Neodymium- in-glass	1.06×10^3	1.17	$\left\{ \begin{array}{l} \text{Q-switched,} \\ \lesssim 100 \text{ ns;} \\ \text{mode-} \\ \text{locked,} \\ \sim \text{ps} \end{array} \right.$	$\left. \begin{array}{l} > \text{MW} \\ > \text{GW} \end{array} \right\}$
Tunable Ga—As diode laser	~ 850	~ 1.46		CW
Ruby	694.3	1.79	$\left\{ \begin{array}{l} \text{Q-switched,} \\ \lesssim 100 \text{ ns;} \\ \text{mode-} \\ \text{locked,} \\ \sim 50 \text{ ps} \end{array} \right.$	$\left. \begin{array}{l} > \text{MW} \\ > \text{GW} \end{array} \right\}$
CW dye laser argon-ion pump	~ 500	~ 2.5		CW
CW mode- locked dye argon-ion laser pump	~ 500	~ 2.5	~ 1 ps	100 watt
Pulsed dye N ₂ laser pump	$\sim 360\text{—}750$	$\sim 3.4\text{—}1.7$	~ 10 ns at 25 p.p.s.	~ 100 kW
Pulsed dye flashlamp pumped Exciplexes and excimers	~ 600	~ 2	trains of 5—200 ps flashes	~ 1 kW
XeF	351	3.53	$\left. \begin{array}{l} \text{pulsed} \\ \sim 25 \text{ ns} \\ \sim 3 \text{ ns} \end{array} \right\}$	\sim MW
XeCl	308	4.03		
KrF	248	5.0		
ArF	193	6.43		
Xe ₂ *	173	7.17		

tions, number density, and refractive indices have been measured.¹⁷⁻¹⁹ The properties of a single microparticle, *i.e.* a single particle with dimensions $\gtrsim 1 \mu\text{m}$ have been determined by laser light scattering in a relatively hostile set of conditions.²⁰⁻²² Thus the passage of a single speck of matter, constituted of metal or metal oxide, through a vacuum with a lifetime $\lesssim 10^{-5}$ s has been observed in the presence of an impulsive electric field $\sim 6 \times 10^7 \text{ Vm}^{-1}$. Such particles play an important role in the failure of the electrical insulation properties of high vacuum. The microparticles are considered to be torn off metal electrodes by the intense field. If a laser beam is used to illuminate a section of the region between electrodes then a detached microparticle traversing this space will scatter the laser radiation, which can be detected using a photomultiplier. The signal produced by the photomultiplier indicates the presence and discloses the velocity of the microparticle from which it is possible to deduce its dimensions, mass, and electric charge. The latter is acquired by the microparticle as it rests on one or other of the test electrodes.

If the laser beam power P is uniformly distributed over its cross-sectional area A (assumed to be a cylinder of diameter d) then a microparticle of cross-section σ moving with velocity v orthogonal to the beam will scatter an amount of energy $P\sigma d/Av$. A photomultiplier with an acceptance area α placed a distance L from the scattering region will receive an amount of energy $P\sigma\alpha/Av4\pi L^2$ if isotropic scattering occurs.

A photomultiplier is a power sensitive device and the power received during the time of transit d/v is $P\sigma\alpha/4A\pi L^2$. This will result in an anode current in the photomultiplier of $I = P\sigma\alpha S(\lambda)G/4A\pi L^2$ and a corresponding voltage impulse V_{pm} into a recording oscilloscope. Here $S(\lambda)$ is spectral sensitivity of the photomultiplier and G its gain. The signal must exceed the electrical noise generated naturally in the photomultiplier. Thus, with a photomultiplier dark current of I_{D} and a signal-to-noise ratio β the minimum detectable particle cross-section is given by

$$\sigma = \beta I_{\text{D}} \left(\frac{A}{P} \right) \left(\frac{4\pi L^2}{\alpha S G} \right)$$

Setting $\sigma = \pi r^2$ for an assumed spherical microparticle of radius r we see that the signal voltage and radius are related by

$$\log r \propto \frac{1}{2} \log V_{\text{pm}}$$

Realistic values of these parameters show that in order to detect a $2 \mu\text{m}$ particle the necessary ratio of noise-power density to laser-power density must be as low as 10^{-12} . This implies a coincidence observation technique to minimize the effects of the noise.

¹⁷ R. M. Friston, A. R. Jones, M. J. R. Schwar, and F. J. Weinberg, *Faraday Symposium Chem. Soc.*, 1973, 7, 183.

¹⁸ A. R. Jones, *J. Phys. (D)*, 1974, 7, 1369.

¹⁹ N. S. Hong and A. R. Jones, *J. Phys. (D)*, 1976, 9, 1839.

²⁰ C. Grey Morgan, Report No. NPA/Int. 66-24, 1966, CERN, Geneva.

²¹ F. Piuze, Report No. TC-L/Int. 72-8, 1972, CERN, Geneva.

²² F. Rohrbach, Doctoral Thesis, Ecole Polytechnique Fédérale de Lausanne, Switzerland, 1971.

This technique is not an absolute method and requires calibration by detecting the signal from a microparticle of known size. Figure 1 shows the data obtained

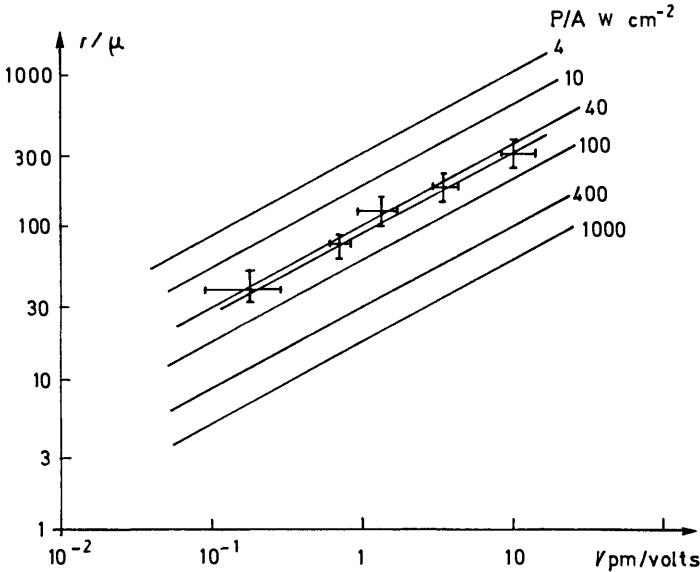


Figure 1 Data obtained for selected bronze micro-spheres of radii 30–400 μm using a free-running ruby laser fired in synchronism with their descent through the beam zone

for selected bronze micro-spheres with radii between 30 and 400 μm using a free-running ruby laser fired in synchronism with their descent through the beam zone. The slope is one-half as suggested by the elementary analysis given above. These data lead to the conclusion that with this arrangement, a power density of 2 kW cm^{-2} , and a minimum detectable signal of 30 mV, corresponding to $\beta = 3$, a 2 μm particle should just be detectable. The subsequent experiments revealed microparticles with the following characteristics which initiated a vacuum breakdown spark.

- Radius $r \sim 6\text{--}10 \mu\text{m}$
- Mass $m \sim 1\text{--}4 \times 10^{-11} \text{ kg}$
- Charge $Q \sim 6 \times 10^7$ electronic charges
- Velocity $V \sim 500 \text{ m s}^{-1}$

The presence of a microparticle followed by a vacuum spark is strong evidence of their role in vacuum breakdown.

4 Detection of Small Traces of Chemicals

In this short review of laser applications to the detection and isolation of ultra-small traces of chemicals we shall preface discussion of the achievements with a brief treatment of the factors which govern the minimum detectable amounts. We

start with the simplest case, namely absorption and transmission of laser radiation through a sample. The variation of the beam intensity transmitted through the sample as a function of wavelength is measured usually by means of heterodyne detection with mixing in a non-linear detector, since this is the most sensitive method for laser light. For strongly absorbing substances, where a substantial fraction (\sim a few percent) of the incident beam energy is absorbed, this is a straightforward method. Maximum absorption occurs in the sample when the energy per quantum of the incident laser radiation is tuned to the energy difference between the allowed energy levels in the absorber and the intensity adjusted to the so-called saturation value I_s . Suppose that the populations of these two levels are designated N_1 for the lower and N_2 for the upper. The laser wavelength λ is tuned to $hc/(E_2 - E_1)$, where E_2 and E_1 are the energies of the upper and lower levels and h is Planck's constant. This resonant radiation can excite atoms (molecules) from state (1) to state (2) so diminishing N_1 and increasing N_2 , and stimulate emission of radiation from the particles already at level (2), so depleting N_2 and building up N_1 . The upward (or downward) rate per atom is $W = \left(\frac{\sigma I_\nu}{h\nu}\right) = c^2 g(\nu) I_\nu / 8\pi h\nu^3 t_s$, where σ is the absorption (or stimulated emission) cross section, $g(\nu)$ is the line-shape function for the levels, I_ν is the laser beam intensity, and t_s is the spontaneous lifetime of the upper level. In propagating through an absorbing sample (travelling in the x direction say) the net transfer of energy from the beam to the sample per unit volume will be $(N_2 - N_1)h\nu$ so that the change of intensity per unit length $dI_\nu/dx =$ change of power per unit volume is given by

$$\frac{dI_\nu}{dx} = - \frac{(N_2 - N_1)c^2 I_\nu g(\nu)}{8\pi\nu^2 t_s} = - \gamma(\nu) I_\nu \quad (1)$$

Thus

$$I_\nu(x) = I_\nu(0)e^{-\gamma(\nu)x} \quad (2)$$

where

$$\gamma(\nu) = (N_2 - N_1)\sigma = (N_2 - N_1)c^2 g(\nu) / 8\pi\nu^2 t_s \quad (3)$$

is the absorption coefficient. Consideration of the reaction rate equations describing the changes in the values of N_1 and N_2 with the variation of intensity I_ν in the sample shows that in the steady state the following expression describes the population difference $(N_2 - N_1)$, viz.

$$N_2 - N_1 \approx \Delta N^0 / [1 + I_\nu \{c^2 g(\nu) / 8\pi h\nu^3\}] \quad (4)$$

where $\Delta N^0 = N_2^0 - N_1^0$ represents the population difference in the absence of the probing laser beam. Thus N_2^0 and N_1^0 are the natural population concentrations when $I_\nu = 0$. We notice in the denominator of equation (4) that the term $\{c^2 g(\nu) / 8\pi h\nu^3\}$ must have the units of $\text{cm}^2 \text{ watt}^{-1}$ to be dimensionally correct, *i.e.* it has the dimensions of $(1/\text{intensity})$. We thus write this intensity as $I_s = 8\pi h\nu^3 / c^2 g(\nu)$ ($= h\nu / 2\sigma t$) and so we can express the population difference $(N_2 - N_1)$ in the presence of the resonantly tuned laser radiation as

$$N_2 - N_1 = \Delta N^0 \left[1 + \frac{I_\nu}{I_s} \right] \quad (5)$$

Now if the laser intensity I_ν is set equal to I_s the population difference is equal to half the unperturbed population difference, *i.e.* when $I_\nu = I_s$, $N_2 - N_1 = \Delta N^0/2$. Further increase in I_ν will reduce the amount of absorption. I_s is, as mentioned earlier, called the saturation intensity. In terms of I_s the absorption coefficient $\gamma(\nu)$ can be expressed as

$$\gamma(\nu) = \gamma_0/[1 + I_\nu/I_s] = \gamma_0[1 - I_\nu/I_s + I_\nu^2/I_s^2 - \dots] \quad (6)$$

Usually, I_ν is much less than I_s so that the rate of change of absorption coefficient γ with intensity, is given by

$$\frac{d\gamma}{dI_\nu} \simeq \gamma_0 \left[\frac{2I_\nu}{I_s^2} - \frac{1}{I_s} \right] \quad (\text{higher terms being neglected}) \quad (7)$$

At a maximum rate of change $\frac{d\gamma}{dI_\nu} = 0$, so that for maximum absorption I_ν should

be half of I_s . Larger values of I_ν would lead to bleaching. Thus, in many investigations, the intensity of the incident laser light is set to half the saturation intensity to achieve optimum absorption and maximum detection sensitivity.

A. Sensitivity and Minimum Detectable Number²³

The minimum number of atoms or molecules n_{\min} which may be detected using this resonance absorption technique may be deduced as follows. During its passage through a uniform absorbing sample of length l the beam intensity diminishes by an amount $\gamma I_\nu l$. In order to be detected this change in beam power must exceed the minimum detectable power P_{\min} of the photo-detector used to monitor the beam in the heterodyne detection arrangement. This in turn depends upon the electrical noise signal generated by quantum fluctuations in the detector and on the local oscillator power—the main laser beam P . Thus, for detection $\gamma l I_\nu > P_{\min}$. Now corresponding to the minimum number of detectable atoms is

$$\gamma = \gamma_{\min} = \gamma_{0\min}(1 + I_\nu/I_s) = \sigma \Delta N^0_{\min}/(1 + I_\nu/I_s)$$

Consequently the condition for detecting n_{\min} is that

$$\sigma \Delta N^0_{\min} l I_\nu / (1 + I_\nu/I_s) = \sigma n_{\min} I_\nu / (1 + I_\nu/I_s) \geq P_{\min} \quad (8)$$

Optimizing by setting $I_\nu = I_s$, and recalling that $I_s = h\nu/2\sigma t$ we find that the minimum number of particles detectable by resonance absorption is

$$n_{\min} = \frac{2 P_{\text{noise}}}{\sigma I_s} = \frac{4t P_{\text{noise}}}{h\nu} \quad (9)$$

²³ V. S. Letokhov, *Optics and Laser Technol.*, 1977, **9**, 217 and 263; *ibid.*, 1978, **10**, 15, 129, 175, 247, and 301.

(These form a series of excellent articles by Professor Letokhov which are essential reading for the laser spectroscopists and photochemists).

Corrections must be applied to this expression for n_{\min} , which is only valid for homogeneously broadened absorption spectral lines. Thus, in a low pressure gas when the linewidths can be made sharper than the Doppler width, n_{\min} must be increased in the ratio of the Doppler width to the homogeneous width of the absorption line.

Again, for molecules, only a fraction f of the species of interest may be in resonance with the laser radiation because of the distribution of occupied rotational and vibrational levels. The value of f can be as small as 10^{-3} for complex molecules so there is a corresponding thousand-fold increase in n_{\min} .

Table 2 gives an indication of the achievable limits n_{\min} for atomic and molecular detection using direct resonance absorption spectroscopy.²³

Table 2

<i>Parameters</i>		<i>Atoms</i>	<i>Molecules</i>
Resonance-tuned wavelength	λ	~ 500 nm (Tunable dye)	~ 5 μ m (CO pumped spin flip)
Upper-state lifetime	t	$\sim 10^{-8}$ s	$\sim 2 \times 10^{-4}$ s
Absorption cross-section	σ	$\sim 4 \times 10^{-12}$ cm ²	$\sim 4 \times 10^{-16}$ s
Detector noise power for 10 mW local oscillator laser input	P_{\min}	$\sim 8 \times 10^{-10}$ W	$\sim 2 \times 10^{-10}$ W
Saturation intensity	I_s	5 W cm ⁻²	0.5 W cm ⁻²
Resonant fraction	f	1	10^{-2}
Minimum detectable number	n_{\min}	$\sim 10^2$	$\sim 3 \times 10^8$

B. Non-resonant Intra-cavity Absorption

Accurately controllable tunability is an extremely useful attribute for atomic and molecular detection but it is not always essential. High detection-sensitivity of a weakly absorbing substance can be attained by inserting the substance inside the laser cavity itself provided the laser has a relatively wide amplification bandwidth $\Delta\nu_{\text{amp}}$ and can hence oscillate simultaneously at many closely spaced frequencies which embrace the absorption bandwidth of the sample as described above. Useful lasers for this purpose thus include neodymium-in-glass and ruby lasers, high-pressure CO₂ lasers and dye lasers all of which exhibit relatively large values of $\Delta\nu_{\text{amp}}$. The method is particularly useful for the detection and measurement of organic compounds. The broad-band absorption lines of organic molecules in the infrared, for example, are made up of the vibrational energy levels. Superimposed on these are the narrow rotational bands which ordinarily cannot be separated even with the use of exceptionally high-resolution spectrometers and very narrow slits, and it is then not possible to produce enough infra-red energy in conventional infra-red lamps for adequate absorption. However, the desired frequencies can be the multimode frequencies generated in a wide bandwidth amplifying medium. Thus the narrow vibrational-rotational absorp-

tion bands can match the narrow laser emission modes resulting in good sensitivity. The principle of intra-cavity spectroscopy is as follows.

The energy spectrum, *i.e.* laser output power ν s wavelength, is measured (a) with the weak gaseous absorber placed in a cell of length l outside the laser cavity between the output mirror and monochromator and power monitor, and (b) with the absorber cell placed inside the cavity. When the cell is placed intra-cavity absorption suppresses those modes whose photon energies coincide with vibrational-rotational levels. The detection requirement is that during the laser flash duration τ the presence of the absorber should cause a reduction in the output beam intensity by say a factor e of the intensity when no absorber is present.

During the time τ photons will be reflected m times between mirrors, *i.e.* $\frac{mL}{c} = \tau$.

During this time the resulting absorption diminishes I by an amount $dI = -\gamma_{in} Iml$, so $-dI/I = m\gamma_{in}l = \left(\frac{c\tau}{L}\right)\gamma l$. Setting $dI/I \sim e^{-1}$ gives the limiting absorption

coefficient γ_{in} when the sample is in the cavity as $\gamma_{in} = L/elc\tau$. With the absorber outside the cavity the absorption coefficient is $\gamma_{out} \sim l^{-1}$, and the resulting gain in sensitivity is the ratio of the two γ 's, *i.e.* $\gamma_{out}/\gamma_{in} \sim ec\tau/L$ which is typically $\sim 10^5$. With a neodymium laser operating in the spiking regime ($\tau \sim 10^{-3}$ s) weak absorption lines in NH_3 , HN_3 , CO_2 , C_2H_2 , HCN , *etc.* due to rotation-vibration transitions with absorption coefficients $\sim 10^{-7} \text{ cm}^{-1}$ have been observed.^{24,25} Continuously operating lasers may also be employed for intra-cavity detection of weak organic absorbers²⁶ in the gas phase and may possibly be extended to solid or liquid samples which can be vapourized in the cavity. Such a technique would represent a major advance in organic chemical analysis. Already the method has been successfully applied to insecticides.²⁷

5 Laser-induced fluorescence

The sensitivity of detection and identification of atoms and molecules by fluorescence has undergone some remarkable advances in recent years as a result of inducing the fluorescence by relatively powerful resonant laser stimulation. The technique is familiar—energy is absorbed from the laser beam at frequency ν_L in causing atomic or molecular excitation. Some of the energy is emitted at a characteristic wavelength ν_F , *i.e.* as fluorescence light, which is detected. Suppose that the laser photons are absorbed in a sample length l and area of section A . The laser power absorbed is $\Delta N^0\sigma IAl$. If we let ϵ be the resulting fluorescence power emitted per watt of laser light absorbed the total fluorescence power produced is $\epsilon\Delta N^0\sigma IAl$. This is emitted isotropically so that if the photon detector subtends a solid angle Ω at the absorbing volume only a fraction $\Omega/4\pi$ of the

²⁴ L. A. Pokhomicheva, E. A. Sviridenkov, A. F. Suchov, L. V. Titova, and S. S. Churilov, *Zhur. Esp. i Teor Fiz.*, 1970, **12**, 60.

²⁵ T. P. Belicova, E. A. Sviridenkov, and A. F. Suchkov, *Kvant Elect.*, 1974, **1**, 830.

²⁶ J. W. Robinson, *Chem. Clin. Analysis*, International Laboratory, 1979, **9**, 55.

²⁷ N. Konjeric, M. Orlov, and M. Tortica, *Spectroscopy Letters*, 1977, **10**, 311.

fluorescence radiation is collected, *i.e.* $\frac{\Omega}{4\pi} \epsilon \Delta N^0 \sigma I A l$ watts. This must exceed the quantum fluctuation noise generated spontaneously in the photo-detector. This amounts to $h\nu_F B / \eta$ where B is the detector bandwidth and η its quantum efficiency. Thus the minimum number of atoms or molecules which can be detected is

$$n_{\min} = (\Delta N^0 A l)_{\min} = \frac{8\pi\nu_F B t}{\nu_L \eta \Omega}$$

using $I = I_s = h\nu_L / 2\sigma t$ for optimum detection. As we have seen in Table 2 this calls for intensities of about a watt cm^{-2} or so.

Laser-induced fluorescence caused by tunable organic dye lasers makes possible the study of so-called invisible reactions in which only ground state products are formed.²⁸ The resonance fluorescence is used to detect the reaction products. The output of the dye laser is tuned through its range of wavelengths and illuminates the sample. Whenever the wavelength resonates with a molecular absorption line the reaction products are excited to an electronic level and subsequently fluoresce. This radiation is focused into a photomultiplier and the intensity measured as a function of wavelength to yield the excitation spectrum. The measured intensities are then used to calculate the relative populations of the product's internal quantum states with the aid of vibrational and rotational intensity factors.

The major factors which govern the technique are firstly that the molecules must fluoresce. Generally this is satisfied for small molecules but there are many polyatomic materials whose excited states decay by radiationless transitions instead of yielding fluorescence. Secondly, the band emission must be analysed spectrally to enable assignment of the quantum numbers to be made and the intensity factors and rotational line strengths to be deduced. This is favourable for the study of diatomic and small polyatomic molecules. Finally, the molecular band emission must lie within the range of tunable lasers. With current lasers spanning the ultraviolet to infrared wavelengths the restriction is rapidly being removed and molecules with band systems in the vacuum ultraviolet are detectable.

In principle, provided there are no sensitivity limitations other than those imposed by the relatively low quantum efficiency and collecting angle of the detector and fluctuations caused by temporal instability in the laser output, the fluorescence method can detect a single atom in a particular excited state.

When atomic trace quantities are to be detected in the presence of other gases of much greater concentrations the saturation intensity produces a background noise signal caused by scattering of the laser light from the non-resonant gas, *i.e.* the so-called Rayleigh scattering. This considerably increases the value of n_{\min} . However, there are methods of overcoming this by using very brief duration laser flashes to induce fluorescence. The flash duration must be less than the relaxation time during which the fluorescence radiation is emitted. Rayleigh scattering thus ceases before the fluorescence signal is detected.

²⁸ R. N. Zare and P. J. Dagdigan, *Science*, 1974, **185**, 739.

Threshold sensitivities for several atoms²⁹⁻³¹ and diatomic molecules³² and radicals³³ have been determined, and assessed in some cases for particular isotopes or particular quantum states. Thus for sodium the detectable density is 10^2 atoms cm^{-3} while for the isotope ^{20}Na the limit is 3×10^3 . Uranium, examined with a CW tunable laser at $\lambda = 591.54$ nm, could be detected with as few as 3×10^3 atoms cm^{-3} . This corresponds to a minimum detectable number of atoms in the irradiation volume of only about 10.

A combination of a molecular beam and tunable laser is a powerful tool for the examination of non-equilibrium distributions of selected quantum states of molecules and for assessing the rate constants of chemical reactions which are not average values for all the states in final equilibrium. Thus, with a sensitivity of 5×10^4 per quantum level per cm^3 , the non-equilibrium distribution of the BaO produced in the reactions between barium and oxygen has been evaluated.³³

When the interaction zone is irradiated by the laser light only a few percent of the molecules in the zone may be in the correct internal quantum state to absorb laser photons and become excited. Of the isotropically emitted fluorescence photons subsequently radiated some 10% or so can fall on a suitably located photomultiplier which would have a quantum efficiency of perhaps ~ 0.1 at the fluorescence wavelength. The system efficiency overall may thus be $\sim 10^{-3}$. In the Ba and O_2 reaction study a pulsed nitrogen laser was used to pump a dye laser at a repetition rate of 10 per second producing a pulse duration of 5 nanoseconds, *i.e.* a duty cycle of only 5×10^{-8} which is very low. Ideally one would use a pulse repetition rate which matches the replacement rate of molecules so that all the molecules are irradiated so giving a greatly enhanced sensitivity. Advances with synchronously pumped CW dye lasers can now increase the sensitivity by orders of magnitude to achieve sensitivities which match those of mass spectrometers.

The vibrational level distributions in barium halide molecules have been examined in this way³⁴ and evidence of non-Boltzmann, *i.e.* inverted, populations has been obtained. The high degree of spectral purity achievable with narrow laser beam lasers enables the light beam to be concentrated to very small diameters. Thus, apart from the relative ease of achieving intensities of I_a or greater, one also achieves very high spatial resolution—approaching the diffraction limit.

The spot diameter d of a narrow (few mm) paraxial beam having a divergence $\theta \sim 10^{-4}$ radians focused by a simple biconvex lens of focal length f (say a few cm) is given by $d \approx f\theta$, so spot sizes of $\sim 10 \mu\text{m}$ are relatively easily achieved. Thus fluorescence spectroscopy can be carried out on fluorescent micro-organisms and used for the detection of antibodies.³⁵

²⁹ W. M. Fairbank, T. W. Hansch, and A. L. Schawlow, *J. Opt. Soc. Amer.*, 1975, **65**, 199.

³⁰ F. C. M. Coolen and H. L. Hagedorn, *J. Opt. Soc. Amer.*, 1975, **65**, 952.

³¹ V. I. Balikin, V. S. Letokhov, V. I. Mishin, and V. A. Semchishen, *Zhur. Esp. i. Teor Fiz.*, 1976, **24**, 475.

³² A. Schulz, H. W. Cruse, and R. N. Zare, *J. Chem. Phys.*, 1972, **57**, 1354.

³³ C. C. Wang and L. I. Davies, *Appl. Phys. Letters*, 1974, **25**, 34.

³⁴ H. W. Cruse, P. J. Dagdigan, and R. N. Zare, *Faraday Discuss. Chem. Soc.*, 1973, **55**, 277.

³⁵ N. R. Berquest, *Scandinavian J. Immunol.*, 1973, **2**, 37

6 Detection using Non-resonance Fluorescence (SONRES)

It is not essential that the wavelength of the fluorescence radiation should match that of the stimulating radiation. Indeed there are sometimes advantages to be gained when they differ significantly. Thus excitation at one wavelength and fluorescence detection at another has resulted in the detection of picogram quantities of caesium in aqueous solution atomized in a graphite furnace³⁶ at atmospheric pressure. This detection of non-resonant fluorescent emission has been effectively combined with saturation in a particularly interesting and powerful development^{37,38} of fluorescence spectroscopy in which the non-resonant fluorescence radiation is collision-induced. Approximately one-sixth of the elements display small energy gap doublets in their spectra—the sodium D lines are probably the best known pair. Excitation of the lower level is achieved by carefully tuned laser radiation. The excited atom undergoes further excitation in an energy transfer collision with an atom of a different species, *e.g.* argon. It is thus transfixed to the upper level by the interaction with the buffer gas, which on de-excitation yields detectable non-resonance fluorescence. This method thus has the considerable advantage of being able to operate at high pressures and hence can be used in conjunction with practical atomization sources such as chemical flames, ovens, and electric furnaces. Furthermore it can be used when there is severe radiation quenching. It has become known as saturated optical non-resonant emission spectroscopy (SONRES).

The basis of the SONRES method may be understood by reference to the specific case of sodium. Figure 2 shows the ground state (0) of the sodium atom,

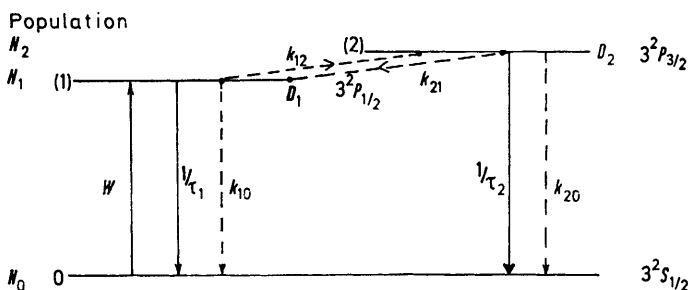


Figure 2 Partial energy level diagram of the sodium atom showing the ground state and lower and upper doublet levels

designated $3^2S_{\frac{1}{2}}$ and the lower (1) and upper (2) doublet levels $3^2P_{\frac{1}{2}}$ and $3^2P_{\frac{3}{2}}$.

The sodium in an atmosphere of argon at high pressure is placed in a laser beam of intensity I_ν , resonantly tuned to the $3^2P_{\frac{1}{2}}$ level so producing excitation at a rate $W = \sigma I_\nu / h_\nu$ per sodium atom, where ν corresponds to the D^1 resonance line at 589.6 nm. Absorption and stimulated emission result in a net rate of

³⁶ J. P. Hohimer and P. J. Hargis, *Appl. Phys. Letters*, 1977, 30, 344.

³⁷ J. A. Gelbwachs, C. F. Klein, and J. E. Wessel, *Appl. Phys. Letters*, 1977, 30, 489.

³⁸ J. A. Gelbwachs, C. F. Klein, and J. E. Wessel, *IEEE, J. Quantum Electron.*, 1978, 14, 121.

change $W(N_0 - N_1)$ in the population N_1 of level 1. In addition, spontaneous decay at a rate τ_1^{-1} where τ_1 is the natural lifetime of level 1, and collisions with the buffer gas at a rate k_{10} further change the population of level 1 by downward transitions. Collisional transfer from 1 to 2 at a rate k_{12} and the reverse process from level 2 at a rate k_{21} , also alter the concentration of atoms in level 1. The atoms in the upper doublet level 2 decay spontaneously at a rate τ_2^{-1} and suffer collisional quenching to the ground state at a rate k_{20} . If the overall detection efficiency of the spontaneous non-resonant emission from level 2 is η the number of pulses recorded per second per atom is $\phi = \frac{N_2 \eta}{N_T \tau_2}$, where $N_T = N_0 + N_1 + N_2$.

The rate equations describing the temporal variation of N_0 , N_1 , and N_2 are

$$\frac{dN_1}{dt} = \frac{\sigma I_\nu}{h\nu} (N_0 - N_1) + k_{21} N_2 - N_1(k_{12} + k_{10} + 1/\tau_1) \quad (10)$$

and

$$\frac{dN_2}{dt} = k_{12} N_1 - N_2(k_{21} + k_{20} + 1/\tau_2) \quad (11)$$

The steady state solution of principal interest, disclosing the fraction of atoms in the upper excited level is

$$\frac{N_2}{N_T} = \frac{[k_{12}/(2k_2 + k_{12})](w/w_s)}{(1 + w/w_s)}, \quad (12)$$

where $w_s = (k_1 k_2 - k_{12} k_{21}) / (2k_2 + k_{12})$; $k_1 = k_{12} + k_{10} + \tau_1^{-1}$; and $k_2 = k_{21} + k_{20} + \tau_2^{-1}$. It is this expression in which we are primarily interested since it determines the non-resonant fluorescent intensity to be detected.

We can represent this schematically to show the saturation effect of increasing intensity on the excitation rate per atom $W = \sigma I_\nu / h\nu$ by noting that equation (12) is of the form

$$N_2 = \frac{A(w/w_s)}{(1 + w/w_s)}$$

The graph shown in Figure 3 of N_2 vs w/w_s indicates saturation of the upper state as w/w_s increases. A represents the maximum achievable population in level 2 and there is little point in reaching this at the expense of considerable laser power. If the intensity I_ν , which yields a value of $A/2$ for N_2 is used, this makes $w = w_s$ and $I_\nu = I_s$ as shown earlier. The form of this curve was confirmed experimentally and good agreement obtained between the calculated saturation intensity of 110 W cm^{-2} and that observed at 140 W cm^{-2} for sodium in argon.

If the intensity I_ν is much larger than I_s the corresponding value of N_2/N_T becomes simply

$$A = \left(1 + \frac{2k_2}{k_{12}}\right)^{-1}$$

and the maximum becomes

$$\phi = (\eta/\tau_2) \left(1 + \frac{2k_2}{k_{12}}\right)^{-1}$$

This serves as a pointer for the selection of atomic candidates for optimized SONRES detection. The radiative lifetime of the upper level should be very short and $k_{12} \gg 2k_2$.

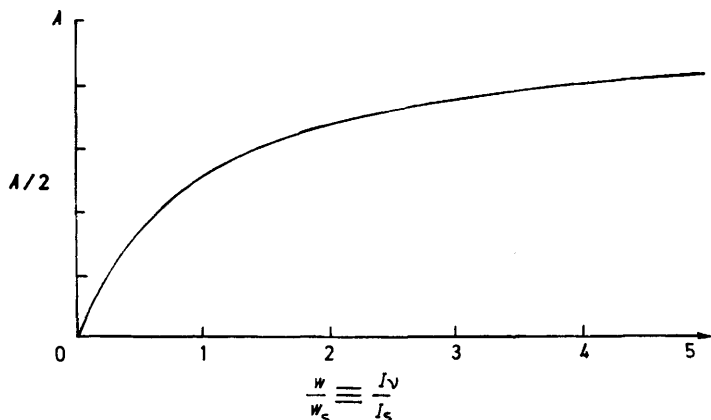


Figure 3 Schematic representation of the saturation effect of increasing intensity on the excitation rate per atom

The equipment used for the detection of sodium is shown schematically in Figure 4. A commercially available CW dye laser is focused into a cell containing

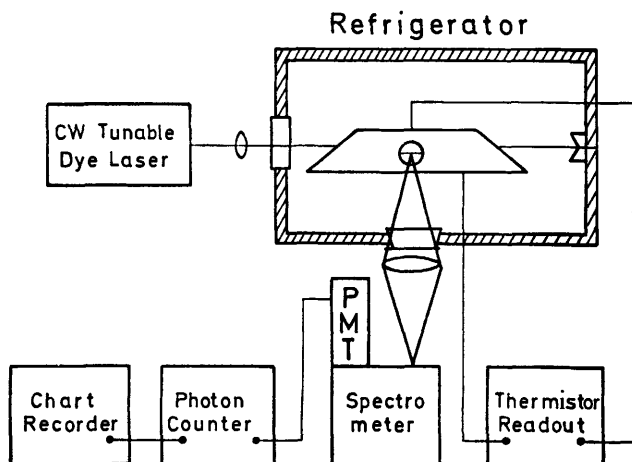


Figure 4 Schematic representation of experimental apparatus employed for SONRES detection of sodium in argon

sodium and argon at atmospheric pressure. The cell is enclosed in a liquid-nitrogen cooled refrigerator and the temperature monitored by thermistors. The non-resonance fluorescence radiation was collected by a lens, focused into the spectrometer and detected by the photomultiplier. The resulting photoelectron pulses were detected by the photon counter and recorder. The spectrometer could be scanned to examine both lines of the sodium doublet. The dye laser emitted 400 mW with an 8 GHz bandwidth at the D_1 line wavelength, and the resulting D_2 line intensity was recorded. Results obtained at -22°C and -25°C are shown in Figure 5.

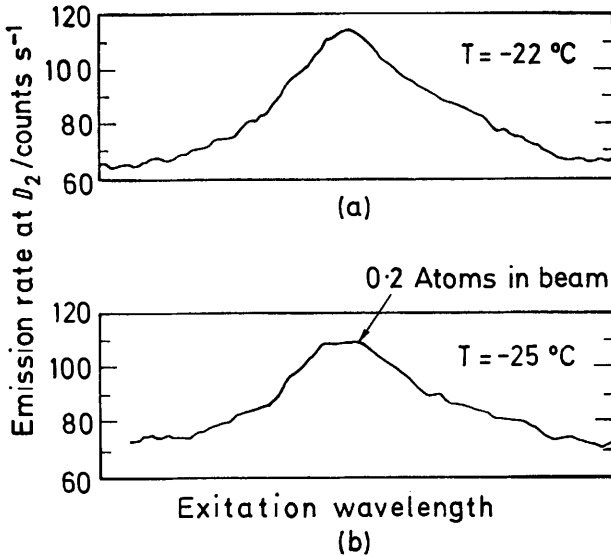


Figure 5 (a) Excitation spectrum of sodium in argon at -22°C . The excitation was near the D_1 line and the fluorescence was monitored at D_2 . The peak of the spectrum is at 589.6 nm and the full-width at half maximum is ~ 20 GHz; (b) a similar spectrum at -25°C

For this specific case of sodium in argon a series of careful measurements covering a wide range of temperature $-35^\circ\text{C} \leq T \leq 40^\circ\text{C}$ yielded atomic densities $1.8 \times 10^{-2} \leq N \leq 10^7$ atoms cm^{-3} in excellent agreement with theoretical thermodynamic data. At the lower temperatures a detection limit ~ 10 atoms cm^{-3} was reported for the observation volume $\sim 10^{-3}$ cm^{-3} , which thus indicates a detection limit $\sim 10^{-2}$ atoms! At -25°C about 180 atoms cm^{-3} were monitored with a signal to noise ratio of ~ 15 representing detection at a level of one part in 10^{17} . The system was thus capable of single-atom detection.

When used to detect the presence of sodium in an air-acetylene flame atomizer where severe radiation quenching occurs the method achieved a detection limit of 10^4 atoms cm^{-3} . This powerful method may be applied, using commercially available tunable lasers, to over 45 elements including heavy metallic ones such as barium, platinum, nickel, lead, uranium, and plutonium.

7 Photon Burst Spectroscopy (PBS)

Another remarkable development of fluorescence spectroscopy stems from using crossed atomic and laser beams in a vacuum in what has become known as photon burst spectroscopy.³⁹⁻⁴¹ This makes it possible to detect an individual atom crossing the laser beam which is tuned to resonance with an allowed optical level. Thus fluorescence is caused and if the atom's velocity is such that the time it takes to traverse the beam is long compared with its natural lifetime it can absorb and emit many quanta before it passes through the beam. This relatively large number of fluorescence photons is called the photon burst.

If the laser beam diameter is d and the atomic velocity orthogonal to the beam is V then the atom crosses the beam in a time $\tau_{cr} = d/V$. In this time it can absorb $\sigma I_p \tau$ joules from the beam—if we neglect the short spontaneous upper state lifetime t . Thus it can emit about $\sigma I_p \tau / h_{\nu F}$ photons. For optimum conditions I_p is set at the saturation value $I_s = h_{\nu L} / 2\sigma t$ so the number of fluorescence photons emitted is $\sim \tau_{cr} / t$. Using typical conditions of $d \sim 0.5$ cm, thermal velocity $V \sim 2 \times 10^4$ cm s⁻¹ for the atoms and with t for the sodium D line as $\sim 1.6 \times 10^{-8}$ s, a beam intensity $I_s \sim 1$ W cm⁻² yields about 10^3 quanta in the photon burst. Each burst thus indicates the passage of a single atom through the CW dye laser beam. The burst is detected by photomultiplier and the output signal is, within microseconds of the transit, digitized, indicating not only the passage of the single atom but also the number of photon pulses detected. The data processing allows suppression of background signals. Thus if a burst contains fewer than say three photon pulses the burst is discounted. This technique is very sensitive. Since several photons from the burst reach the detector every time an atom traverses the laser beam the sensitivity is much greater than the single-photon counting efficiency. In one experiment the probability that an atom at thermal speed produced at least three photons during a $10 \mu\text{s}$ transit time was 76% with the overall single photon detection efficiency of 5%. The chance for the same event to occur due to random background radiation is only about 4×10^{-6} . Even allowing for photomultiplier dark current makes this $\sim 10^{-4}$. The detection limit is about 10 atoms per second through the beam. This corresponds to a density of 0.2 atoms cm⁻³. Again this represents single atom detection. Since a continuous wave dye laser is employed the system is continuously sensitive and can indicate the presence of an atom within microseconds. Only very low powers are needed, about 0.1 W cm⁻², and since only excitation takes place the atoms under investigation remain intact. It does of course require an atomic beam and thus a high vacuum. Currently the method seems limited in application to some alkali and alkaline earth elements.

³⁹ G. W. Greenlees, D. L. Clark, S. L. Kaufman, D. A. Lewis, J. F. Tonn, and J. H. Broadhurst, *Optics Comm.*, 1977, 23, 236.

⁴⁰ G. W. Greenlees, D. L. Clark, S. L. Kaufman, D. A. Lewis, J. F. Tonn, and J. H. Broadhurst, *Laser Focus*, 1978, 14, 9.

⁴¹ D. A. Lewis, J. F. Tonn, S. L. Kaufman, G. W. Greenlees, J. H. Broadhurst, and D. L. Clark, *Bull. Amer. Phys. Soc.*, 1977, 22, 579.

8 Resonant Ionization Spectroscopy (RIS)

One of the most striking advances in laser spectroscopy of trace amounts which is having far-reaching consequences in chemical and physical analysis is Resonance Ionization Spectroscopy. This is a very versatile and powerful technique capable of detecting atoms in specific quantum states and single atoms or molecules in the presence of a relatively high pressure gas background of foreign atoms. It is highly selective and has good spatial and temporal resolution. It can also be used to cause photo-dissociation of molecules and to generate a spatially well defined population of atoms in their ground state at a controllable pre-determined time.⁴² It provides an excellent tool for studying the microchemistry of reactive atoms⁴³ free from the perturbing influence of wall effects. It is based upon resonance photoionization of the selected species by multiple photon absorption. Single atom detection based upon multiple photon ionization is of course closely related to the question of isotope separation and the preparation of ultra-pure chemicals. RIS exploits the fairly large power available from pulsed tunable lasers to excite selectively and then ionize, either by two- or three-photon absorption, all the atoms in a well defined region. The electrons so created are detected in a proportional counter which indicates the presence of the selected atom. The underlying principle for single atom detection by RIS is as follows. The fairly powerful output from a pulsed tunable laser resonantly excites a ground state atom to a selected intermediate state lying more than half-way between the ground state and ionization continuum. A second photon from the laser can then photoionize it from the intermediate state and convert it into an electron-ion pair. Laser fluences $\sim 1 \text{ J cm}^{-2} \text{ cm}$ can saturate the process, *i.e.* ionize all selected atoms in the beam. Alternatively use can be made of two synchronously pulsed tunable lasers to excite the ground state atom, firstly to a lower selected quantum state, using one laser photon $h\nu$, then to a second selected bound state by a photon $h\nu_2$ from the second laser, and finally into the continuum by a photon from either.

The case of two-photon ionization is shown in Figure 6 which illustrates two-photon absorption leading to ionization and the competitive processes of spontaneous decay from level 1 to level 2, chemical reactions due to collisions between excited atoms in level 1 and ambient gas at rates τ_{21}^{-1} and β respectively. Detailed consideration of the rate equations describing the population in the levels as functions of laser intensity and duration shows that in order to obtain saturation, *i.e.* to ionize all the selected atoms in the irradiated volume, the product of the photoionization cross-section of level 1 and the photon flux must greatly exceed the sum of the destruction rates $\beta + \tau_{12}^{-1}$ so that the rate of photoionization exceeds the loss rates to spontaneous radiation and collisional deactivation, and the product of the photoionization cross-section and photon fluence must be much larger than unity. In order to effect single caesium atom

⁴² G. S. Hurst, M. G. Payne, M. M. Nayfeh, J. P. Judish, and E. B. Wagner, *Phys. Rev. Letters*, 1975, 35, 82.

⁴³ M. G. Payne, G. S. Hurst, M. H. Nayfeh, J. P. Judish, C. H. Chen, E. B. Wagner, and J. P. Young, *Phys. Rev. Letters*, 1975, 35, 1154.

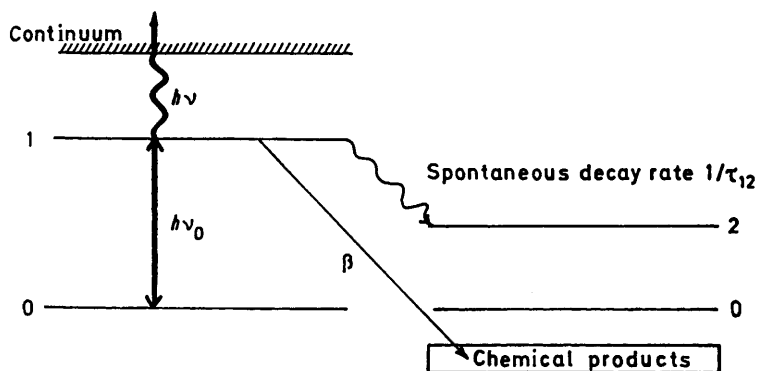


Figure 6 Two-photon ionization

detection these conditions were satisfied by using a flash-lamp pumped dye laser yielding fluence of a few millijoules tunable over a wide range with a linewidth of 7 nm and duration of $1.2 \mu\text{s}$. The beam could be focused to exceed 200 mJ cm^{-2} . Figure 7 indicates the experimental arrangement. The laser beam is directed

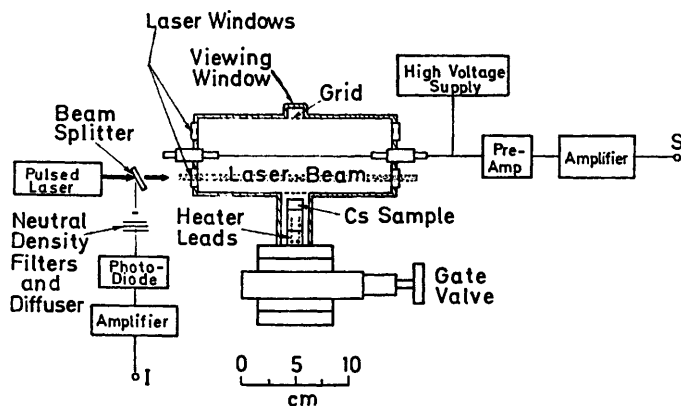


Figure 7 Schematic of the experimental arrangement of a flash-lamp pumped dye laser (Reproduced by permission from *Appl. Phys. Letters*, 1977, 30, 229)

through a proportional counter (ionization cell) containing 90% argon and 10% methane at a pressure of several hundred Torr. The caesium atoms diffuse into the cell at a very low rate from a side arm. Each caesium atom arriving in the laser beam is photoionized and since the proportional counter detects each photoelectron so liberated each ionized atom is detected. By this means single caesium atoms in the presence of 10^{19} argon atoms were recorded. By changing the relative position of the probing beam and the caesium source large concentration gradients were detected indicating directly that ground state chemical reactions were rapidly occurring.

The application of RIS is currently being extended to include studies of photoionization cross-sections of excited atomic states and reaction rates of ground-state and excited species with other reactive elements.

There is no doubt that RIS offers many exciting opportunities in analytical chemistry as well as in physics.⁴⁴⁻⁴⁷

⁴⁴ G. S. Hurst, M. H. Nayfeh, and J. P. Young, *Phys. Rev. (A)*, 1977, **15**, 2283.

⁴⁵ G. S. Hurst, M. H. Nayfeh, J. P. Young, M. G. Payne, and L. W. Grossman, 'Laser Spectroscopy', ed. J. H. Hall and J. L. Carlsten, Springer Verlag, Berlin, 1977.

⁴⁶ L. W. Grossman, G. S. Hurst, M. G. Payne, and S. L. Allman, *Chem. Phys. Letters*, 1977, **50**, 70.

⁴⁷ L. W. Grossman, G. S. Hurst, S. D. Kramer, M. G. Payne, and J. P. Young, *Chem. Phys. Letters*, 1977, **50**, 207.