# 3 Light Sources

## 3.1 Introduction

Among the properties desired in an SPC excitation source are high intensity, repetition rate variable from khz to 100 MHz, complete polarization of radiation, tunability over some 500 to 600 nm, wavelength-independent pulse shape, perfect reproducibility of pulse shape and intensity, and picosecond pulse widths. This ideal source would also be inexpensive and relatively easy to transport from one laboratory to another. Such a source does not, of course, exist. In general, sources that fulfil eminently some of these conditions have severe disadvantages in other respects. For instance, synchrotron storage rings furnish extremely stable sub- nanosecond pulses at repetition rates up to 40 MHz. But the intensity per pulse is quite low and, for the majority of workers, the facility is, to say the least, inconvenient to use. Again, mode-locked lasers furnish high intensity picosecond pulses at MHz repetition rates but are not easily tunable and can be very expensive. The spark gap discharge lamp can be tuned easily but suffers from lack of intensity in a narrow spectral bandwidth, furnishes pulses of relatively long duration, and does not enjoy long-term stability of pulse profile.

In this chapter, we shall discuss in more detail the three sources already referred to. We shall not consider the non-optical sources that have occasionally been used in SPC, such as pulsed X-rays (Phillips and Swank, 1953; Henry and Helman, 1972) and electron bursts (Bennett *et al.*, 1965). Nor shall we describe the ingenious methods of pulse generation based upon a continuous light beam impinging on a rotating mirror system, which have attained little popularity in SPC instruments, presumably because of low intensity per pulse (Garbury *et al.*, 1957) and poor pulse shape reproducibility. For a review of these methods the reader is referred to the paper by Jones (1964). The discussion of synchrotron radiation will be brief, since, although it is in many ways an attractive excitation source, it is almost impossible for most research workers to use it on a regular basis for lifetime measurements.

Prospective purchasers of SPC equipment will clearly have to opt for the quality of items for which they have funds available. In Appendix 3.A1 we list suppliers of excitation sources, from whom prices may be obtained. Other important factors such as wavelength tunability, reliability, ease of service, radio frequency noise generation, etc., will be considered in each section. At this stage, it might be useful to point out that, in general, a sample that is likely to cause complications because it is liable to undergo photodecomposition will do so just as readily under flash lamp as under laser excitation, because of the longer data collection times required for flash lamps.

## 3.2 Storage Ring Radiation

The classical mechanism by which electrons in an accelerating field lose energy is by the emission of electromagnetic radiation. In a circular accelerator such as a synchrotron or a storage ring, the accelerating field is created by magnetically constraining the electrons to travel round a closed path; the consequent centripetal acceleration leads to the emission of synchrotron radiation (SR). In actual synchrotron machines electron energies are high ($>m_0c^2$, $m_0$ = electron mass) and relativistic effects result in SR emission in a well-defined distribution of directions about the tangent to the electron orbit. Most of the intensity from a point at the source is confined within a cone having a small half-angle given by $m_0C^2/E \approx 0.1$ milliradians with respect to the tangent. Therefore, for these electrons, with $E$ in the GeV range, almost all the emitted light lies in the plane of the electron orbit (Lopez-Delgado *et al.*, 1974).

As an excitation source for SPC the storage ring is more suitable than the synchrotron. In the latter electrons are continuously injected and accelerated; during the accelerating cycle the properties of the radiation are varying rapidly with time. In a storage ring, on the other hand, electrons are pre-accelerated, injected into the ring and then maintained in a stable orbit in an ultra-high vacuum chamber ($10^{-10}$ Torr) by a constant magnetic field. Therefore the properties of the radiation important in SPC, such as pulse repetition rate, pulse width, angular distribution, etc., remain constant over many hours of continuous operation.

Storage ring radiation has the following important features:

(1) It is a continuum from the hard X-ray region to 10 μm (see Fig. 3.1).
(2) It provides a small natural aperture with relatively high photocollection efficiencies.
(3) The repetition rate of the pulses (depending on the particular machine) can be as high as 400 MHz.
(4) The pulse width, which depends on the length of the circulating electron bunch, can be as low as 150 ps and is usually $\leqslant 1$ ns.
(5) The radiation is 100% linearly polarized with the electric vector in the orbital plane.

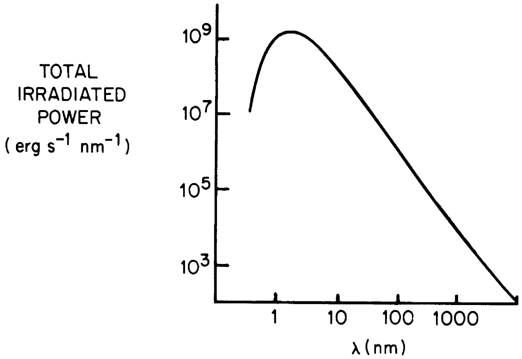


*Figure 3.1* Calculated wavelength distribution of radiation in the ACO synchrotron source at 540 MeV electron energy and 100 mA circulating current (adapted from Lopez-Delgado *et al.*, 1974).

(6) The electron distribution in the bunch can be calculated exactly for a real accelerator. It is nearly Gaussian. The photon distribution in the pulse is also nearly Gaussian. Statements that the pulse shape in real machines is exactly calculable are probably over-optimistic.
(7) There are strong theoretical and experimental grounds for believing the pulse shape to be wavelength independent.
(8) Interpulse optical noise is negligible.
(9) Intensities per pulse delivered to the sample have been calculated to be $1.5 \times 10^4$ photons with 4 MHz repetition rate at 300 nm (Lopez-Delgado *et al.*, 1974). This intensity (which has not been verified experimentally) is greater than that furnished by flash lamps, but less than pulsed laser intensities.

It will be seen that storage ring radiation has many features that recommend it for the SPC experiment. In particular, the wide and easy wavelength tunability, polarization, narrow pulse width, and invariance of pulse shape with wavelength are highly attractive properties. The greatest disadvantage of the source is its inconvenience. The machine may be quite far from the user's place of work with consequent difficulties in experimental programme planning and sample transport. Furthermore, in many storage ring facilities, organization of user time leaves something to be desired, with the result that measurements have to be carried out hurriedly. It is probably preferable, on the whole, to employ a less inconvenient source for regular lifetime determinations. Nevertheless, in view of the merits of SR radiation, one would be well advised, before purchasing or constructing one's own SPC instrument, to ascertain the user facilities at the nearest storage ring machine and to consider whether one's needs could be met by one or two visits a year to the machine. Storage rings in operation at present as well as those under construction are listed in Table 3.1.

## 3.3 Flash Lamps

### 3.3.1 Introduction

The first flash lamp for use in single photon counting was constructed by Malmberg (1957), and its application was described by Brody (1957). Almost all flash lamps designed since then consist, essentially, of two metal electrodes enclosed in a gas, which, when a sufficiently high voltage is applied through a charging resistor, undergoes periodic dielectric breakdown providing flashes of light. Flash lamps may be classified into four basic types according to the pressure of the filling gas and the method by which the low voltage electrode is connected to earth. Details peculiar to each type will be given in Section 3.3.2. Some practical considerations, common to all types, are discussed first.

First, in most lamps the gas is enclosed in a sealed chamber, which should be fitted with one or two optical windows. The windows must be sealed tightly in order to prevent leakage but should also be easily demountable so that they may be cleaned conveniently. In glass-bodied lamps black wax is preferable to epoxy resins for sealing purposes since it requires only moderate heat to soften and can be removed easily with trichloroethane. Less messy than either is a threaded glass tube onto which a plastic ring is screwed bearing down on the optical flat. The seal is made by means of an O-ring between the flat and the rim of the threaded tube. If a photomultiplier provides the trigger pulse for the electronics the lamp should have two optical flats. Suprasil is the usual window material. For excitation in the vacuum ultra-violet, magnesium fluoride or lithium fluoride discs give transmission down to about 110 nm and are not particularly difficult to handle. Lithium fluoride, however, may form colour centres. In high pressure lamps the attachment of windows is more difficult and the method chosen should first be thoroughly tested at the appropriate pressures. If the spark is to be struck exclusively in air at 1 atm., windows are not necessary.

Electrode sputtering is the main cause of loss of window transmittance, for which reason the window should not be placed too close to the electrode gap. A distance of 2 cm between window and gap has been found satisfactory (Lewis *et al.*, 1973). Platinum as an electrode material tends to deposit relatively heavily on the windows; hence thoriated tungsten is now more common. Although preferable to platinum, tungsten electrodes usually develop, over many hours of operation, a tip of deposited material, which reduces the length of the spark gap and hence the intensity. Flashing stability

*Table 3.1* Selected parameters of storage rings which are used as synchrotron radiation sources. $E_0$: electron energy, $R$: bending radius, $E_c$: critical energy, $T_0$: circulation time, $N$: harmonic number, $T_{r.f.}$: period of r.f. field, $t$: bunch length.

| | $E_0$/GeV | $R$/m | $E_c$/keV | $T_0$/ns | $N$ | $T_{r.f.}$/ns | $t$/ns |
|---|---|---|---|---|---|---|---|
| SURF (Washington, USA) | 0.25 | 0.83 | 0.041 | 17.5 | 2 | 8.8 | |
| TANTALUS (Stoughton, USA) | 0.24 | 0.64 | 0.048 | 31.4 | 1 | 31.4 | 1–4 |
| INS-SOR (Tokyo, Japan) | 0.3 | 1.1 | 0.054 | 57.8 | 7 | 8.3 | |
| ACO (Orsay, France) | 0.54 | 1.11 | 0.31 | 73.5 | 2 | 36.7 | 0.8–1.4 |
| BROOKHAVEN (USA) VUV Ring | 0.7 | 1.9 | 0.40 | 170.3 | 9 | 18.9 | |
| BESSY (Berlin, West Germany) | 0.75 | 1.8 | 0.52 | 208.3 | 26 | 8.0 | 0.01–0.13 |
| | | | | | 104 | 2.0 | |
| VEPP 2M (Novosibirsk, USSR) | 0.67 | 1.22 | 0.54 | 59.9 | 20 | 3.3 | |
| ALADDIN (Stoughton, USA) | 1.0 | 2.08 | 1.1 | 295.0 | 15 | 19.7 | |
| ADONE (Frascati, Italy) | 1.5 | 5.0 | 1.5 | 349.7 | 3 | 111.7 | |
| DCI (Orsay, France) | 1.8 | 3.82 | 3.4 | 316.4 | 8 | 39.5 | |
| SRS (Daresbury, UK) | 2.0 | 5.55 | 3.9 | 320.5 | 160 | 2.0 | 0.2 |
| PHOTON FACTORY (Tsukuba, Japan) | 2.5 | 8.33 | 4.1 | 598.8 | 285 | 2.1 | |
| BROOKHAVEN (USA) X-ray ring | 2.5 | 6.8 | 5.1 | 568.2 | 30 | 18.9 | |
| DORIS (Hamburg, West Germany) | 3.5 | 12.1 | 7.8 | 961.5 | 481 | 2.0 | 0.13 |
| SPEAR (Stanford, USA) | 4.0 | 12.7 | 11.1 | 781.2 | 279 | 2.8 | 0.08–0.4 |
| CHESS (Cornell, USA) | 8.0 | 88 | 12.8 | 2222.0 | 1111 | 2.0 | 0.1 |
| VEPP-4 (Novosibirsk, USSR) | 7.0 | 29 | 26.0 | 1250.0 | 227 | 5.5 | |

and pulse profile are also degraded. The deposit, thought to arise from impurities extracted from the tungsten by the strong electric field (Berlman *et al.*, 1968), must be removed. Application of the high voltage to the electrodes when the lamp is completely evacuated may reduce the deposit but it will usually be necessary, at some stage, to remove the electrodes and clean them with emery paper. Removable electrodes in glass-bodied lamps may be force fit through Teflon stop-cocks. For machineable materials swagelock or similar fittings are satisfactory. In either case, provision should also be made for adjustment of the interelectrode spacing.

The electrode to which the high voltage is applied is generally machined to a point while the other electrode is either rounded or flat ended. It would appear that the reason is purely empirical, these being the shapes that give best performance. If both electrodes are pointed, the arc wanders and the flash does not stabilize, whereas if both are rounded a fuzzy arc is generated, again yielding a flash that cannot be timed precisely. When the electrodes have been cleaned it is necessary to apply the high voltage to the lamp for at least one hour before commencing measurements. During this time the arc will be seen to wander round the earthed electrode until finally "burning a hole" in it, at which stage the discharge arcs between two fixed points and the flash profile is stable. It will frequently be found that the arc does not stabilize; in these cases a slight adjustment to the arc gap should be made. When the high voltage is first applied to a newly-filled lamp, the electrodes of which have not been cleaned, the lamp should be allowed to run for at least fifteen minutes so that the plasma can reach equilibrium conditions. It is also worthy of note that unstable performance has been reported in misaligned electrodes, that is when the electrodes are not collinear (Lyke and Ware, 1977).

For most designs of lamp, it is advisable to have attached a connection for evacuation and gas filling. Operations can then be performed without removing the lamp or if possible, the back plate from the lamp housing. It is not necessary to evacuate with a diffusion pump but it is vitally important to incorporate an oil trap between the rotary pump and the lamp. Liquid nitrogen is of course most effective, but even a molecular sieve of silica gel granules will suffice. Oil vapour in the plasma region causes grossly unstable operation. Unstable operation may also result if the filling gas is not of high purity (Lyke and Ware, 1977).

For ease of alignment the lamp should be mounted in such a way that the position of the arc can be adjusted, preferably without removing the access plate from the housing. A simple X–Y stage should be satisfactory for this purpose. It should of course be borne in mind that wires carrying extremely high voltages are attached to the electrodes and must not be allowed to come into contact with earthed components. If the electrodes are carried in teflon stop-cocks there will always be the temptation to adjust the arc gap while the high voltage is applied. This temptation should be resisted. Furthermore, when the high voltage has been switched off the stray capacitance in the circuit should be discharged before current-carrying components are touched. Discharge is most conveniently achieved by connecting the high voltage to earth through a screw driver while holding the insulated (plastic) handle. A further hazard associated with hydrogen- or deuterium-filled lamps is the possibility of an explosion if air has leaked into the electrode chamber. Glass-bodied lamps, in particular, may shatter under the stress of such an explosion with the consequent possibility of injury to the user. Therefore, when the high voltage is first applied to a lamp that has not been filled for some time, the access plate of the housing should be securely in position.

After construction or purchase the lamp should be tested for leaks and if any are found they must be eliminated. With hydrogen or deuterium as filling gases in low pressure lamps leakage may be more severe. Small leaks can be detected by monitoring the pressure in the spark gap chamber during operation. The initial rise in pressure as the plasma heats is usually followed by a slight drop to a steady value. If the pressure continues to drop gas is probably leaking from the chamber. Slightly larger leaks, through which air diffuses into the chamber, will lead to a change in the colour of the arc from an initial blue to a purple-violet.

In all types of flash lamp stray or added capacitance, $C$, is charged through a resistor $R$ and discharged through the arc gap, causing the flash (Fig. 3.2). In general the duration of the flash is proportional to the product $RC$. Consequently for a narrow pump pulse profile the capacitance must be as

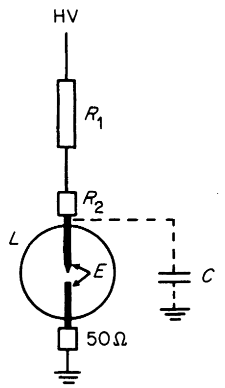


*Figure 3.2* Circuit representation of free-running flash lamp. HV, high voltage; $R_1$, resistor or resistor string; $R_2$, resistor; $C$, capacitor (stray or added); L, lamp envelope; E, electrodes.

small as possible. It can be reduced by replacing a single bulky resistor $R$ with two resistors $R_1$ and $R_2$ one of which is physically small (Yguerabide, 1965). By attaching $R_2$ as close as possible to the electrode, $C$ and consequently the flash duration is reduced. By increasing $C$, usually by adding a high voltage capacitor between the tip of the high voltage electrode and earth, increased intensity per flash can be attained at the expense of short pulse width.

Low pressure lamps, which are usually operated under partial vacuum, tend to collect foreign vapours in the flash chamber. These vapours may be absorbed into the electrodes, survive the initial pumping and flushing and be outgassed at the high plasma temperatures. We have already referred to pulse instability resulting from the rotary pump oil vapours. Another source of instability is the plasticizer that may be present in polythene tubes connecting the lamp to the pump or even in the material of the lamp itself.

Lamps made from a machineable plastic material, Rexolite*, give stable operation over quite long periods, but recently a ceramic material has been reported to give better performance (Lyke and Ware, 1977). This high vacuum dielectric material, although easily machineable, requires careful handling because it tends to crack if screws or tube fittings are tightened too much. Like Rexolite and metal it is less fragile than glass, and does not require epoxy or black wax sealant for the windows. In lamps constructed from machineable materials the electrodes can be secured by means of nylon straight thread fittings with O-ring seals (see Fig. 3.7). Nylon, teflon, flexible metal, or glass tubing should provide the connection between pump and lamp on the lamp side of the trap. Yet another source of contamination is vacuum grease that may be used on joints in the vacuum system or on O-rings that seal on the windows. Wherever possible grease vapour should be trapped; there is generally no need for grease on O-rings. Since apiezon grease has higher fluorescence than silicone grease the latter is recommended for the vacuum joints. Greaseless joints, however, are preferable.

Flash lamp housings will be discussed in Section 3.3.6 as will r.f. suppression. Pulse intensities will be discussed in Section 3.3.4. It should be mentioned here that undistorted pump pulse profiles have seldom been published owing to the difficulty of deconvolving the detector response from the measured instrument response function. Almost all the available data suggest that flash lamp pulses have a low intensity, relatively long lived tail, although the secondary peak observed in most instrument response functions is almost entirely a result of photomultiplier effects (Lewis *et al.*, 1973).

*Rexolite is manufactured by Atlantic Laminates, Franklin, New Hampshire, USA.

## 3.3.2 Four basic types of lamp

### *3.3.2(a) High pressure, ungated lamps*

In an ungated, or free-running, lamp one of the electrodes is connected directly to earth and, as Fig. 3.2 illustrates, the lamp is essentially a relaxation oscillator. The discharge takes place at or near the breakdown voltage of the gas. Pulse width and repetition rate are determined by the time constant, $R \times C(R = R_1 + R_2)$.

Filling gas pressures in excess of 1 atm. are referred to as high; those reported in high pressure lamps vary between 1.5 atm. and 30 atm. Usually the lamp remains attached to the pressurizing system during operation but it may (with some risk to the handler) be sealed off from the gas filling line by means of, for example, a special crimping tool (Yguerabide, 1965). In the earlier designs of this type of lamp the spark was struck between mercury wetted electrodes (D'Alessio *et al.*, 1964; Yguerabide, 1965) but more recently mercury has been dispensed with. In the design of Hundley *et al.* (1967), illustrated in Fig. 3.3, thoriated tungsten electrodes are sealed into a quartz cylinder which is surrounded by a copper cylinder. It will be noticed that the charging resistors are placed inside the pressurized region in order to reduce surface breakdown. It is more usual to cool the resistor, placed outside the lamp body, by for example, immersing it in oil cooled by a water jacket (Rayner *et al.*, 1976).

In order to minimize the duration of the flash, the stray capacitance, $C$, should be as small as possible. As was mentioned already, a short high voltage electrode appears to yield narrower pulses, as does an increase in the width of the metal container in the region of this electrode. Coaxial electrode enclosures are also reported to yield slightly narrower pulses owing to reduced capacitance between the high voltage electrode and earth. In all types of flash lamp it is a general rule of thumb (admitting of some exceptions) that the optical pulse width is proportional to the width of the electrode spacing. Spacings in high pressure lamps are usually quite small ($<1$ mm) since a narrow arc gap induces discharge at reasonably low voltages. However, the pulse widths in low pressure and high pressure lamps seem to be comparable. Some optical pulse width measurements have been made with very fast detectors such as photodiodes or image converter tubes. As a guide to the duration of pulses from high pressure discharge the results of D'Alessio *et al.* (1964) (FWHM = 0.5 ns for hydrogen at 18 atm., 1–10 kV, 0.7 mm arc gap), Yguerabide (1965) (FWHM = 0.5 ns for hydrogen at 20 atm.; 0.5 ns for air; 1 ns for xenon at 20 atm., all with 0.2 mm arc gap), Hundley *et al.* (1967) (FWHM = 1.25 ns for oxygen at 6 atm., 12 kV, 0.762 mm arc gap) and Wahl *et al.* (1974) (FWHM = 0.97 ns for deuterium at 15 atm.) may be quoted. Pulse profiles from this type of lamp are shown in Fig. 3.4.

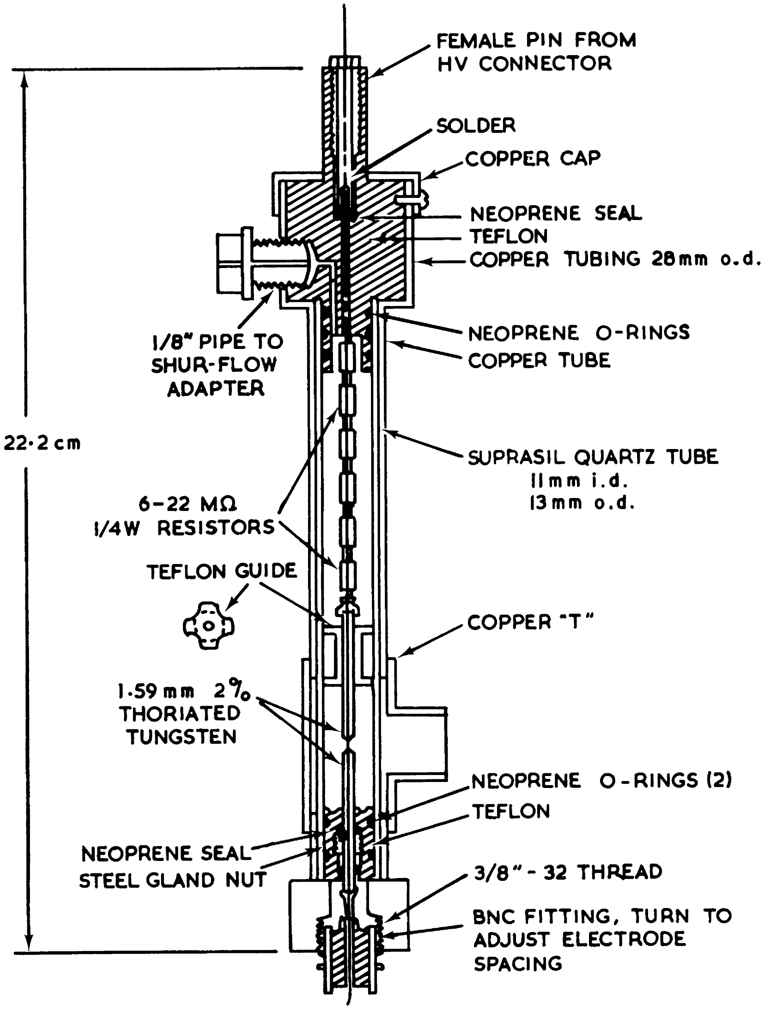


*Figure 3.3* Schematic diagram of a high pressure free-running flash lamp (after Hundley *et al.*, 1967).

In free-running lamps the pulse repetition rate cannot be varied at will. It is determined by the applied voltage, the breakdown voltage (electrode spacing, gas and pressure) and the *RC* time constant. Firing as fast as 50 000 pulses a second may be attained, although at the higher frequencies the power per pulse is drastically reduced. For this reason high pressure lamps are, in general, operated at lower repetition frequencies than gated lamps. Typical operating frequencies lie in the range 1 kHz to 15 kHz. Intensity per pulse will

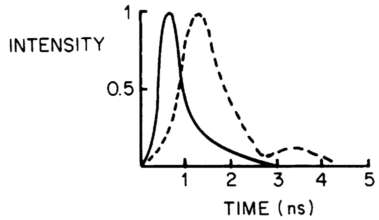


*Figure 3.4* Time profiles of pulses generated in a high pressure discharge (with a small amount of detector convolution effects). —, $H_2$ at 20 atm. (adapted from Yguerabide, 1965); ..., $O_2$ at 6 atm. (adapted from Hundley *et al.*, 1967).

be discussed in Section 3.3.4. The voltage required to break down the gas depends on pressure and electrode spacing. Voltages ranging between 2 kV and 25 kV have been reported.

A number of gases are suitable for high pressure operation, the most common being $D_2$, $H_2$, $N_2$, $O_2$ and air. It is surprising that oxygen, which does not produce stable pulses in a discharge at low pressures, seems to perform well when the pressure exceeds 5 atm. The spectral output of the $O_2$ high pressure lamp (Fig. 3.5(a)) is more or less flat from 250 nm to 600 nm. Hydrogen has a similar spectrum (Fig. 3.5(b)). Nitrogen, which shows its characteristic line spectrum at low pressures (see Fig. 3.8), produces at high pressures a continuum from 200 to 400 nm (Thomaz *et al.*, 1975; Yagi *et al.*, 1978). Air has essentially the same spectral output as nitrogen but the time characteristics of the light pulses differ somewhat. It is likely that, in high pressure lamps, the pulse shape is independent of wavelength, although experimental evidence for this statement is slight.

High pressure lamps are probably less common now than formerly, presumably because of the inconvenience associated with pressures in excess of atmospheric. In addition, gated lamps offer more flexibility of operation, the repetition rate being adjustable by the simple means of a frequency control on the thyratron grid pulser. One commercial manufacturer of SPC equipment (Applied Photophysics Ltd.) has discontinued its high pressure free-running lamp in favour of the low pressure gated variety. The reason is not clear but may perhaps be connected with instabilities encountered in the high pressure discharge. Recently a high pressure lamp has been marketed by Horiba Ltd. The performance of the lamp has not yet been tested "in the field", but is reported to be very stable.

### *3.3.2(b) Low pressure, ungated lamps*

For this type of lamp, the charging circuit is again as illustrated in Fig. 3.2, but the discharge chamber is filled to 1 atm. or less with the flashing gas. Low

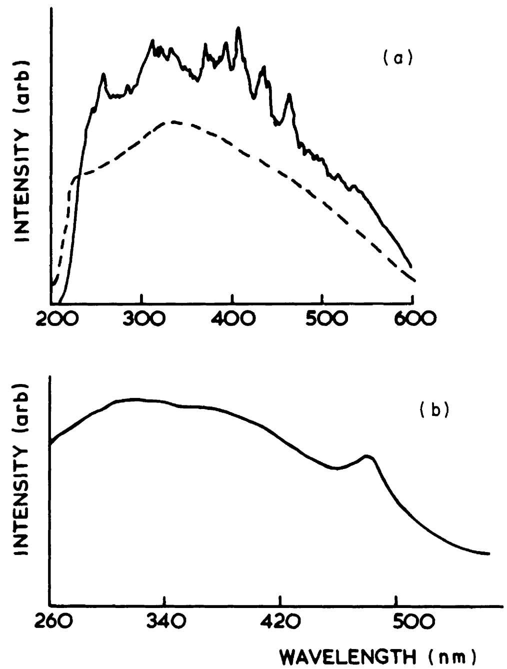


*Figure 3.5* Measured spectra of light emitted from high pressure flash lamps. (a) $O_2$ at 6 atm. (—) (adapted from Hundley, 1967); (b) $H_2$ at 20 atm. (adapted from Yguerabide, 1972). Both spectra are uncorrected for the spectral response of the detecting system (monochromator and 1P28 PM). The relative sensitivity of the 1P28 PM is plotted as the dotted line in (a).

pressure free-running lamps are, therefore, simple and relatively inexpensive to construct and operate. The charging resistor $R(=R_1+R_2$ in Fig. 3.2) is again fairly large (20–30 MΩ) but because of the low pressures applied, high voltages are usually less than 10 kV. Consequently, r.f. noise generation is likely to be less severe. A simple design for this type of lamp that can be made quite easily from pyrex glass is shown in Fig. 3.6 while a design for which some machineable insulator (such as Rexolite or ceramic) would be suitable is shown in Fig. 3.7. In the first design the tungsten electrodes are force fit through the teflon; if the seal is not complete a bead of epoxy or Torr-seal can be applied at the point of exit of the metal from the teflon. In this design the arc gap is adjusted merely by turning either one of the stop cocks. The window can be attached with black wax or epoxy. In the second design a disc of the insulating material is made to bear down on the window which forms a seal with an O-ring slotted into the lamp body. The swagelock fittings are of the compression type and can be of brass or, preferably, nylon.

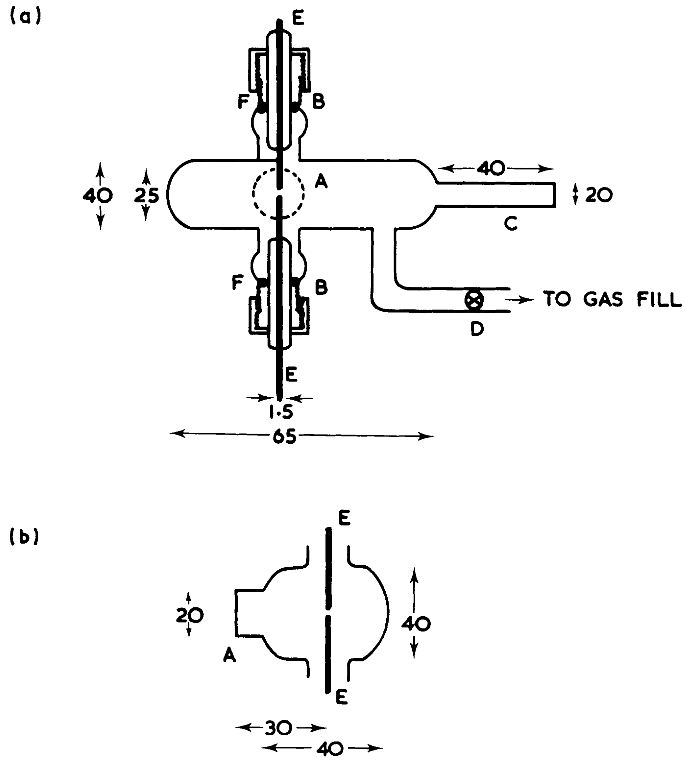


*Figure 3.6* Design of low pressure Pyrex flash lamp (not drawn to scale: all dimensions in mm). A, Suprasil optical flat; B, Youngs PTT/10 stop cocks; C, arm for mounting; D, stop cock; E, tungsten electrodes; F, O-rings (included in B). (a) Front view; (b) side view.

Typical operating conditions for the lamp illustrated in Fig. 3.6 are: R, 20 MΩ; applied high voltage; 6 kV; arc gap, 2 mm; gas pressure, 0.5 atm. With deuterium as the filling gas these conditions produce a repetition rate of about 90 kHz and a pump pulse profile having a FWHM of 3 ns. (This is crudely estimated by subtracting 1 ns from the FWHM of the measured instrument response function.) Narrower pulses and higher repetition rates can be attained by decreasing the arc gap but rates in excess of 100 kHz seem to yield reduced overall intensity and unstable operation. We would stress that these conditions are suitable for the specified design and a 20 MΩ charging resistor. Instrument response functions of FWHM as low as 800 ps have been obtained in a commercial flash lamp, Ortec model 9352 (no longer on the market), with air as the filling gas (Leskovar *et al.*, 1976).

There need be no difference in construction between low pressure lamps

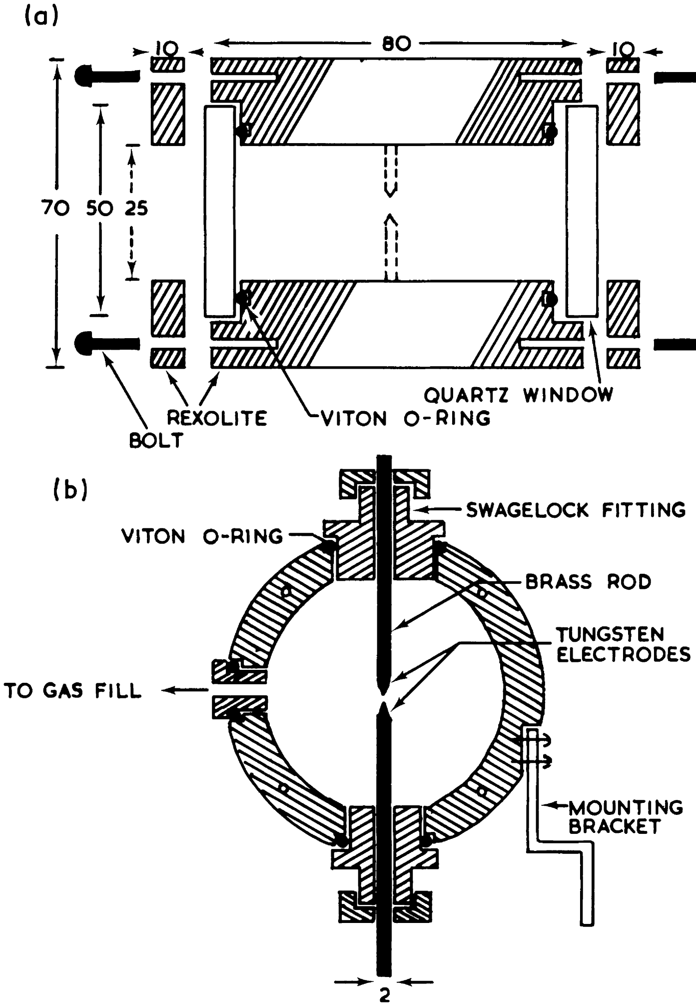


*Figure 3.7* Design of low pressure flash lamp that can be machined from plastic (not drawn to scale). (a) Side view cross-section; (b) rear view cross-section. All dimensions in mm.

whether they are free running or gated. Therefore, the designs illustrated in Figs 3.6 and 3.7 could serve equally well for thyratron-gated lamps. Filling gases that are suitable for low pressure operation are also the same. As was mentioned, oxygen does not perform well at low pressures. On the other hand, air yields an optimum performance at pressures of 1 atm. or less. The low pressure spectrum of air, which consists mostly of emission from the $C^3\pi_u$

$\rightarrow B^3\pi_g$ transition of molecular nitrogen, is illustrated in Fig. 3.8(a). Emission is mainly between 300 and 400 nm. Air, even at low pressures, is frequently found to be troublesome to work with since it causes electrode sputtering. As a consequence the flash repetition rate becomes less stable, and a deposit, formed on the window and electrodes, leads to drastically reduced intensity. Window blackening may not be severe if the distance between electrode gap

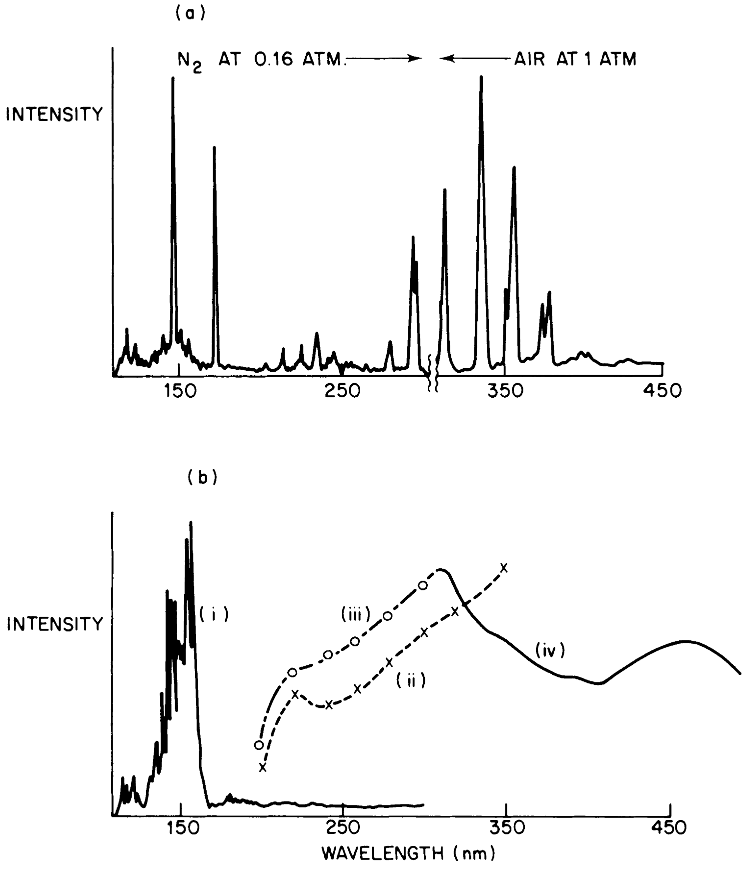


*Figure 3.8* Measured spectra of light emitted from low pressure flash lamps. (a) $N_2$. Measured in different laboratories and uncorrected. Spectra in either side of the wavelength indicated by the arrow are not normalized relative to each other. From 110 to 310 nm correction factor not known. From 310 to 450 nm rough correction can be achieved with 1P28 sensitivity curve (Fig. 3.5(a)).

(b)(i) $H_2$ at 0.1 atm. (adapted from Lyke and Ware, 1977); (ii) $H_2$ at 0.16 atm. (adapted from Berlman *et al.*, 1968); (iii) $D_2$ at 0.16 atm. (adapted from Berlman *et al.*, 1968); (iv) $D_2$ at 1 atm. (adapted from Badea and Brand, 1979).

and window is reasonably large. Leskovar *et al.* (1976) obtained a stable repetition rate by flushing a steady flow of dry air through the discharge chamber during operation and by cleaning the electrode tips after every ten hours of operation. Essentially the same spectral output and increased intensity can be obtained from nitrogen but at the cost of a broader pulse profile. In addition, the exact conditions of arc gap, high voltage and pressure necessary to obtain stable operation with nitrogen are difficult to determine. Carbon monoxide, which has a highly structured emission between 150 and 250 nm, is reported to give rise to particularly loathsome reaction products (Lyke and Ware, 1977) and cannot be recommended.

Hydrogen and deuterium are probably the most common discharge gases in low pressure lamps. Although the intensity from these gases is less than that available from air or nitrogen, the pulse width is narrower and stable operation can be attained over a wide range of operating conditions. The approximate relative spectral output of these gases is illustrated in Fig. 3.8(b). The intensity distribution in $H_2$ and $D_2$ is thought to result from transitions from lower vibrational levels of the $1s\sigma 2s\sigma^3\Sigma g$ state to a repulsive $1s\sigma 2p\sigma^3\Sigma u$ state (Coolidge and James, 1939). Although spectrum (i) is not corrected for the wavelength response of the detection system, the intensity of the many line spectrum below 170 nm is known to be in excess of the continuum extending from 200 to 600 nm. The relative intensity in this continuum is flatter than is indicated by the uncorrected spectrum. Published spectra with peaks in the wavelength range from 300 to 400 nm (e.g., Brody, 1957) probably result from air contaminated hydrogen plasmas rather than from, as has been suggested by Knight and Selinger (1973), impurities in the tungsten. As spectrum (iii) illustrates, the emission from $D_2$ is more intense than that from $H_2$; this enhancement pertains at all wavelengths. Optical pulse widths from both gases are the same so that $D_2$, were it not so expensive, would obviously be recommended over $H_2$.

### *3.3.2(c) Low pressure, gated lamps*

Low pressure lamps are usually gated, in accordance with the charging circuit illustrated in Fig. 3.9. With discharge triggered by the thyraton, voltages in excess of the gas breakdown voltage can be applied with a consequent increase in the pulse intensity. In addition, the pulse repetition rate can be independently adjusted by means of an oscillator driving the thyratron pulser. A lamp of this type was described by Malmberg as early as 1957. Gated lamps are probably still the most common type of flash lamp and are the type offered by three of the commercial companies marketing SPC instruments (see Appendix 3.A1). One design of lamp body is illustrated in Fig. 3.10. This lamp, together with the thyratron, will be housed in a larger

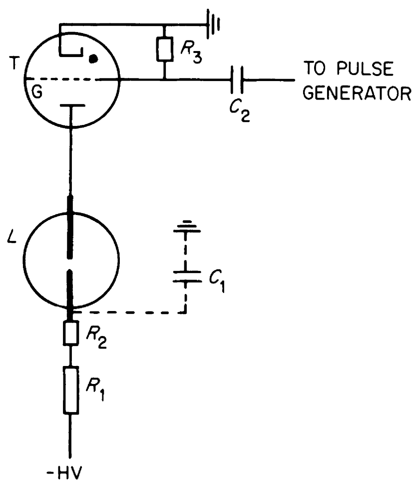


*Figure 3.9* Low pressure flash lamp gating circuit L, lamp; T, hydrogen thyratron; G, grid of thyratron; $C_1$, stray capacitance; $C_2$, 0.01 $\mu$F; $R_1$, *c.* 1 M$\Omega$; $R_2$, *c.* 0.5 M$\Omega$; $R_3$, 22 k$\Omega$; HV, 4–10 kV.

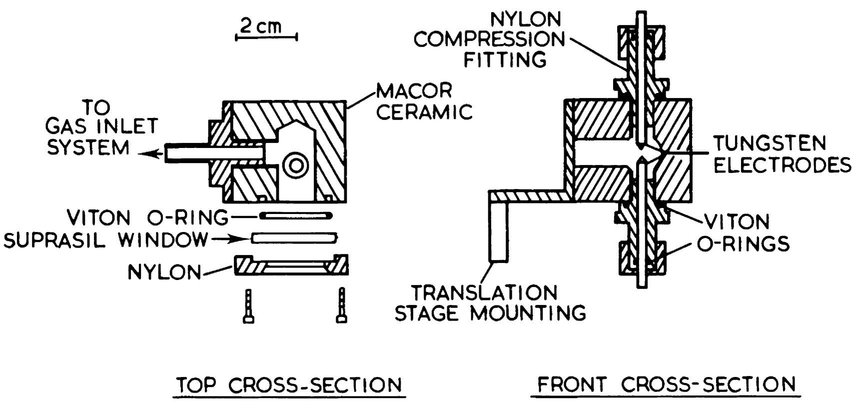


*Figure 3.10* Design of low pressure flash lamp constructed from MACOR ceramic (adapted from Lyke and Ware, 1977).

metal box. In a more compact design, illustrated in Fig. 3.11, the thyratron is coaxial with, and physically close to, the electrode. The lamp body is of metal, removing the need for a separate metal housing.

Among the thyratrons in common use are the E, G and G Models HY2 (rated at 8 kV) and HY6 (16 kV), ITT Model 7621 and English Electric Model FX 2530/6777. The grid pulse for both the HY2 and HY6 should be

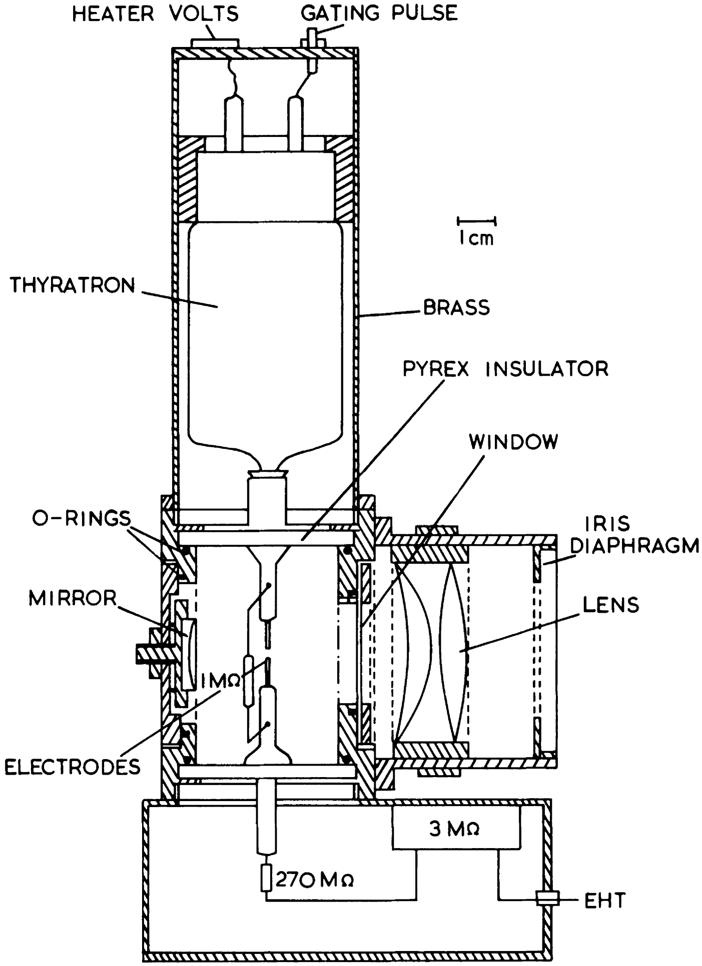


*Figure 3.11* Design of low pressure triggered flash lamp constructed from brass. Connection to gas filling system and window for trigger photomultiplier are not shown. The resistor across the electrodes is reported to improve pulse stability (adapted from Birch and Imhof, 1981).

from 100 V to 300 V amplitude with a rise time of about 20 ns and a FWHM of about 50 ns. A circuit for producing the required pulses has been described by Halpern (1974) and includes 24 p–n diodes (thyristors) in series, each having a forward breakdown potential of about 15 V. A circuit diagram has been given by Knight and Selinger (1973) and is illustrated in Fig. 3.12. For all thyratrons the plate breakdown factor (repetition rate × peak anode

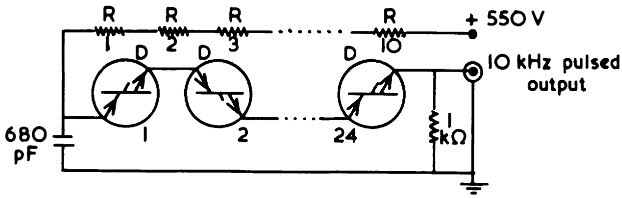


*Figure 3.12* Design of pulse circuit for gating thyratron. R, 5 kΩ, 2 W; D, Western Electric 443A thyristor diode (after Knight and Selinger, 1973).

voltage × peak anode current) should not be exceeded. Even if the circuit can deliver pulses to the grid at a faster rate the breakdown factor may place an upper limit on the pulse repetition rate. In two commercial SPC instruments (Applied Photophysics Ltd., Edinburgh Instruments Ltd.) the thyratron can be operated at up to 200 kHz but pulse widths at these high repetition rates are extremely large (6–10 ns). The critical factor causing this effect seems to be the limited currents available from the flash lamp high voltage supply (West, 1981). In any case, the best all round performance for gated lamps is achieved with the repetition rate in the range 20–50 kHz. It is possible to derive the trigger pulse for the counting electronics from the thyratron pulser but, because of instabilities in the firing circuit, it is preferable to time the actual flash (see Section 3.3.5). It should be possible to limit the flashing rate instability to less than 10 Hz in 50 kHz.

In hydrogen thyratrons of the type employed in flash lamp circuits the gas reservoir must be maintained at a certain temperature by means of an externally supplied heater voltage. This voltage is 6.2 V a.c. for the ceramic–metal thyratrons HY2 and HY6. It can be derived from the mains through a simple step-down transformer. However, if the mains voltage is not stablized it is convenient to route it through a Variac transformer before input to the 6.3 V transformer. In this way a slightly higher heater voltage can be supplied to the reservoir and observed malfunctioning resulting from insufficient heating avoided. It is also advisable to route the heater voltage through a passive r.f. filter (see Section 3.3.6). Heat generation by the thyratron may result in high temperatures inside the lamp housing. Therefore a small fan is sometimes attached to the back or side wall. It should be noted, however, that the ventilation holes constitute an outlet for r.f. leakage. In addition, care must be taken to avoid overcooling the thyratron. Unless resistors, capacitors or the lamp body are being damaged by overheating, therefore, fan cooling is best avoided. While no evidence has been reported connecting optical pulse width with the lead length from earth electrode to thyratron, on general principles of optimum conditions for pulse transmission the lead should be kept as short as is compatible with the geometry of the housing. Thyratrons are quite robust and should yield years of operation before failure. Nevertheless, whenever lamp malfunctioning is observed the thyratron should be rigorously tested for internal mechanical failure.

There has been some discussion concerning the factors that determine the pulse shape in triggered lamps. Berlman *et al.* (1968) and Birch and Imhof (1981), on observing a narrowing of the time profile at increased pressures, concluded that the sub-nanosecond decay times resulted from collisions between excited and unexcited molecules, higher pressures causing greater frequency of collisions. Collisional quenching would also account for the decrease in intensity sometimes observed at higher pressures. Ware and co-workers on the other hand, on observing an almost negligible shape change in pulses from the many-line $H_2$ spectrum at 170 nm and the continuum at 220 nm postulated that the emitting states are quenched so far that the observed time profile is determined by complex plasma processes (Andre *et al.*, 1979). No definite conclusion can be reached until a reliable method for determining the actual pulse shape (as opposed to the instrument response function) has been devised. At least part, if not all, of the long tail sometimes observed in instrument response functions, which, it has been suggested, results from recombination of electrons and positively charged molecules (Malmberg, 1957), is generated in the detection photomultiplier. It is likely however, that with $N_2$ and air, for which this tail is much more pronounced, recombination effects are important. In addition, since the air pump pulse is narrower than the nitrogen pulse and the intensity is also considerably reduced, oxygen is likely to be quenching at least some of the nitrogen emission processes. It is interesting to note, however, that with the lamp illustrated in Fig. 3.11 an instrument response function with FWHM as short as 1.2 ns has been measured for nitrogen.

Of the four gases that are most popular for low pressure lamps, $H_2$, $D_2$, $N_2$ and air, $H_2$ and $D_2$ probably yield the narrowest pulse profiles. However, it is difficult to reconcile all the reported values of FWHM. We have already mentioned the FWHM of 0.8 ns reported for the instrument response function of an air lamp (Leskovar *et al.*, 1976) which is shorter than the FWHM of the actual pulse profile calculated for $H_2$ by Andre *et al.* (1976). Birch and Imhof (1981) obtained similar FWHM values in instrument response functions from $H_2$ and $N_2$ (0.95 and 1.2 ns, respectively) whereas a difference of almost a factor of 4 was reported by Birks *et al.* (1962). Again one laboratory has reported a broader FWHM for $D_2$ pulses compared with $H_2$ pulses (Berlman *et al.*, 1968) whereas another has reported no difference (Lewis *et al.*, 1973; Lyke and Ware, 1977). Until a complete set of results has been obtained with the newest generations of flash lamps and detection components, perhaps the most reasonable conclusion should be based on the results from a single lamp operated under accurately controlled conditions. If such a basis is accepted the widths of pulse profiles from $H_2$, $D_2$ air and nitrogen are in the ratio 1:1:1.25:1.5 (Lewis *et al.*, 1973).

As the discussion in Section 2.3 makes clear a variation in pump pulse shape $E(\lambda,t)$ with wavelength is a potentially serious problem, particularly if the photomultiplier response is also wavelength dependent. Pulse shapes from air and nitrogen lamps are indeed wavelength dependent. Fortunately, the wavelength dependence of the response in many PM tubes can be approximated by a simple time shift which can be incorporated in the deconvolution routine. Since shift routines are not without their own problems it is advisable, whenever the nature of the experiment makes it possible, to observe the fluorescence at a wavelength as close as possible to the excitation wavelength. Alternatively, the experimental correction of Szabo and co-workers, described in Section 2.3, can be applied. It is generally believed that the pulse shape of $H_2$ or $D_2$ is independent of wavelength in the range 200 to 400 nm. Direct evidence for this belief is however lacking. Methods of deducing pulse profiles, $E(\lambda,t)$, from measured instrument response functions, $P(\lambda,t)$, are discussed in Section 4.4. The result of application of one of these methods to the $H_2$ pump pulse profile between 170 nm and 220 nm is shown in Fig. 3.13. Owing to the limited resolution of the method, it is not possible definitely to attribute the observed difference in the second decade of intensity to a physical cause. It is clear, however, that over almost a decade and a half of intensity the pulse profiles are identical.

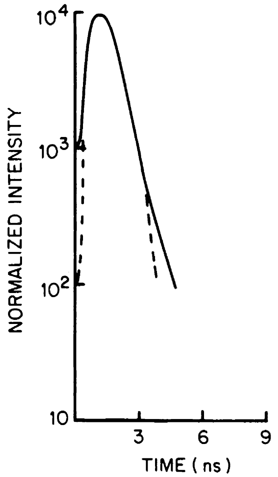


*Figure 3.13* Pulse profile for $H_2$ flash lamp ....., 170 nm; ——, 220 nm (adapted from Andre *et al.*, 1979).

*3.3.2(d) High pressure, gated lamps*

Although high pressure lamps are thought to yield a more intense flash than low pressure lamps, their flash repetition rates, which are not independently variable, are generally lower. An obvious modification in these lamps is to gate the gas breakdown with a thyratron. The plate breakdown factor, however, discussed in the previous section, imposes a limit on the repetition rate that can be achieved for a given pressure. Successful gated operation of $N_2$ at 2 atm. has been reported (Birch and Imhof, 1981) but intolerable instabilities have been observed when gating is attempted at higher pressures (O'Connor, 1977). At time of writing it appears that gating is most successful for pressures less than or in the region of 1 atm.

## 3.3.3 Operating conditions and performance

The pump pulse reproducibility is of critical importance in the SPC experiment. It is essential, therefore, to determine the operating conditions (applied high voltage, pressure, arc gap, charging resistor and capacitance, and flash repetition rate) that yield optimum performance for a given lamp body, electrode material and filling gas. Since optimum conditions change not only from one design of lamp to the next but even among different lamps of the same design, the choice of these conditions is largely an empirical process. Each operating variable is adjusted independently (as far as possible; increased pressures will usually require increased voltages for gas breakdown) and the pulse shape, as observed on an oscilloscope and as measured in the instrument response function, is noted. In this section we mention briefly some points that might be overlooked by a first time user. Some of these points have been discussed in more detail previously (e.g., Berlman *et al.*, 1968; Birch and Imhof, 1981).

Since pulse characteristics are strongly dependent on applied high voltage, the power supply should incorporate a voltage regulator. If it does not, the mains voltage to the power supply should be regulated. In home-built supplies, any a.c. ripple superimposed on the applied d.c. voltage should be eliminated. In gated lamps at repetition rates of about 30 kHz the current drawn by the arc is about 2 mA, well within the capability of most power supplies. Instability of pulse shape at higher repetition rates may result in part from inability of the power supply to deliver the requisite current. The optical power is much more dependent on applied voltage in gated lamps than in free running lamps. In all low pressure lamps optimum stability is usually found at an applied voltage less than that required for maximum intensity. A high charging voltage may also produce increased r.f. noise.

Increased pressure is observed to lead to a narrowing of the pulse profile in low pressure lamps. As with intensity, however, the narrowest pulse is not necessarily the most stable. In addition, as pressure is increased above a certain value, intensity decreases. These effects can be attributed to quenching of the emitting state although it is worthy of notice that pulse narrowing does not persist when pressure is raised above about 1 atm. In general, optimum pressures for $H_2$ or $D_2$ lie in the range 1/3 to 2/3 atm., whereas for air and nitrogen the optimum pressure seems to depend strongly on the particular lamp.

As might be expected, at smaller arc gaps intensities and pulse widths are reduced, and r.f. noise generation increases, especially if the applied voltage is raised in an effort to recover intensity. In low pressure lamps arc widths of from 2 to 3 mm are standard, whereas for high pressure lamps widths range from about 1.5 mm to less than 1 mm. As was stated previously, the electrode tips should be kept clean. It is sufficient to remove them from the lamp and rub them with emery paper when a whisker appears. When erosion has become severe, the high voltage electrode should be re-ground to a point.

The flash repetition rate to be adopted will depend to some extent on the capabilities of the thyratron. It should also be noted that at high repetition rates intensity per pulse drops drastically, with the result that overall intensity per second reaches a maximum at some intermediate value of the repetition rate. It has already been noted that pulse widths increase as repetition rate increases. In most gated lamps repetition rates in the range 20 kHz to 60 kHz appear to yield optimum performance.

In general, flash lamps are run on stray capacitance. Measurements of the capacitance range from 6 pF (Lewis *et al.*, 1973) to 20 pF (Schuyler and Isenberg, 1971). If it is desired to increase intensity, a capacitor, rated at the voltage applied to the electrode, is connected between the high voltage electrode and earth. Intensity should be roughly proportional to capacitance ($C$) according to the formula

$$E = \tfrac{1}{2}CV^2, \tag{3.1}$$

where $E$ is the electrical energy dissipated and $V$ is the applied voltage. It is not known whether the optical energy is linearly dependent on capacitance, but it has been reported that a considerable increase in intensity resulted when a 30 pF capacitor was added in a gated lamp (Ware and O'Connor, 1977). The stability of the pulse profile was maintained while the FWHM of the instrument response function increased from 2 ns to 10 ns. Although the type of charging resistor is not critical, its wattage rating must be chosen so that it does not overheat at the applied high voltage. If carbon film resistors are used they can be grouped in parallel pairs and added in series until the desired resistance is attained. A close check should always be kept on resistors to confirm that breakdown due to overheating has not occurred.

A useful diagnostic of flash lamp performance is the count rate as measured on a counter timer. A stable repetition rate is not, of course, a requisite in the SPC experiment; however, instabilities are usually accompanied by pulse-to-pulse profile changes, which can seriously distort the collected data. If the repetition frequency shows large fluctuations the trigger pulse should be examined for jitter on an oscilloscope.

### 3.3.4 Power

There have been relatively few measurements of the absolute intensity of flash lamp pulses. It is well established however that intensity in nitrogen is greater than in air, which is in turn over an order of magnitude more intense than hydrogen. Deuterium delivers about twice the power of hydrogen. It is worthy of note that optical power does not increase as the square of the applied voltage (see Equation 3.1) as has been reported (Malmberg, 1957); the dependence appears to be more or less linear (Birch and Imhof, 1981).

*Table 3.2* Experimentally determined intensities for various types of flash lamp.

| Gas | Type of lamp[a] | Photons per flash | Flash repetition rate/kHz | Reference[b] |
|---|---|---|---|---|
| $H_2$ | LP, G | $4 \times 10^8$ | 3 | 1 |
| | HP | $4 \times 10^8$ | 20 | 2 |
| | LP, G | $8 \times 10^8$ | 25 | 3 |
| | LP, G | $4 \times 10^8$ | 25 | 4 |
| $D_2$ | LP, G | $1.3 \times 10^9$ | 3 | 1 |
| | LP, G | $1.6 \times 10^9$ | 25 | 3 |
| Air | LP, G | $2 \times 10^{10}$ | 25 | 3 |
| | LP, G | $1.4 \times 10^{10}$ | 25 | 5 |
| | LP, F | $3 \times 10^6$ | 15 | 6 |
| | LP, F | $<5 \times 10^6$ | 90 | 5 |
| $N_2$ | LP, G | $8 \times 10^{10}$ | 25 | 3 |
| | LP, G | $1.2 \times 10^{11}$ | 15 | 7 |
| | LP, G | $2 \times 10^{10}$ | 25 | 4 |
| $O_2$ | HP | $4 \times 10^9$ | 20 | 2 |
| | HP | $6 \times 10^{11}$ | 2 | 8 |

[a] LP, G = low pressure, gated.
LP, F = low pressure, free-running.
HP = high pressure.
[b] References: 1. Berlman *et al.*, 1968; 2. Yguerabide, 1972; 3. Lewis *et al.*, 1973; 4. Birch and Imhof, 1981; 5. Phillips and O'Connor, 1981; 6. Leskovar *et al.*, 1976; 7. Stuart and Kirk, 1977; 8. Hundley *et al.*, 1967.

Optical output is usually determined by ferrioxalate actinometry (Hatchard and Parker, 1956). A less troublesome, though less reliable, procedure is measurement with a calibrated radiometer. In Table 3.2 we have assembled some representative data on flash lamp intensities. We have attempted to correct published figures so that the numbers in column 3 represent intensities per pulse integrated over all wavelengths and emitted into $4\pi$ steradians. Since data collection times in the SPC experiment depend on the total number of photons incident on the sample we have also given the flash repetition rate at which the measurements were made.

Give the errors inevitably accompanying chemical actinometry and those associated with our corrections based on the published geometry details (sometimes incomplete) there is in general rather good agreement among the results of different laboratories. It is interesting to notice that high pressure lamps operated at high repetition rates do not offer enhanced intensity over low pressure lamps. On the other hand as the results for oxygen indicate it is more efficient to operate a high pressure lamp at low repetition rates. As can be seen from the data for air, gating produces orders of magnitude more intensity in low pressure lamps.

It would appear from these data and the considerations discussed in previous sections that gated lamps provide the most satisfactory all round performance among flash lamps. High pressure free-running operation does not result in increased intensity and is less flexible as far as varying the operating parameters is concerned. Moreover, high pressure lamps are less simple to construct and operate safely.

### 3.3.5 The trigger pulse

With flash lamp excitation the trigger pulse in the SPC experiment is usually derived from an antenna, which detects an r.f. signal every time the lamp flashes, or from a photomultiplier which views the lamp directly, or through a fibre optic cable. If the lamp is thyratron-gated a synchronous pulse may be available from the thyratron grid pulser electronics. However, because the lamp may occasionally fire without a gating pulse or fail to fire when the gating pulse is delivered it is no longer common practice to trigger with the pulser sync. pulse.

Antennae are particularly convenient to operate since they require only a BNC bulk head connector on the lamp housing, a 50 Ω load resistor and a short length of coaxial cable. The centre conductor on the cable is connected to the bulkhead connector. The stiffness of the cable is then sufficient to support it so that the other end is about 3 to 6 cm from the lamp body. The 50 Ω resistor is connected between a convenient earthing point on the housing and the central conductor of the coaxial cable at the lamp end.

Photomultipliers such as the RCA 1P28 are ideal for trigger pulse purposes since they are easy to accommodate together with their voltage divider network in a small box attached to the side or back of the flash lamp housing. The interstage resistance can be constant (e.g., 22 kΩ) and the anode is terminated in 50 Ω. In order to avoid saturation effects neutral density filters (or wire mesh) may have to be inserted between the lamp and the photomultiplier window.

## 3.3.6 Lamp housings and r.f. suppression

A radio frequency electrical signal is always generated at the time of arc gap discharge. Because this is picked up in the fluorescence channel electronics, it can distort the observed instrument response functions and decay curve (see for example, Grinvald, 1976). If the interference is severe the instrument response function will appear to narrow and a ripple will be observed in the decay curve. Less severe interference may not be obvious from a visual inspection of the recorded data but will lead to erroneous data analysis since a mathematical correction for this distortion is not possible. The fluorescence PM and electronics must therefore be shielded from r.f. noise. Somewhat reduced r.f. interference is expected for flash lamps of the type illustrated in Fig. 3.11 which are of coaxial design and are not constructed from an insulating material (Birch and Imhof, 1981). Since it is more convenient to construct the lamp from glass, ceramic, or plastic we give here some details of r.f. suppression that have been found helpful in the past. For a further treatment of this topic the reader is referred to Morrison (1967).

The flash lamp housing should be designed in such a way that the number of apertures, through which r.f. can leak, is as small as possible. In addition, unless the apertures can be fitted with a waveguide the length of which is about twice as long as the diameter, they should be as small as possible. Solder gasket seals should be inserted between bulkhead electrical connectors and the metal of the lamp housing. Paint should be cleared from areas where there is metal-to-metal contact. It may be impossible to follow these directions in all respects since the lamp housing must accommodate not only an aperture for light exit but also a mounting stage for the lamp, an input for high voltage and either an antenna bulkhead connector or an aperture for viewing by the trigger photomultiplier. In addition, it may also have a thyratron mounting stage and bulkhead connectors for input of the thyratron grid pulse and heater voltage, a gas inlet, fan, shutter, etc. However, if screw holes are kept as small as possible and well-contacted wire mesh covers the photomultiplier viewing point or fan vent, r.f. leakage can be reduced to negligible levels.

Welding is recommended for all joints in the housing except at one side, usually the back, where a removable plate is necessary to allow access to the inside of the housing. This plate should be stepped and have a lip wide enough to allow insertion of a solder or indium gasket inside the screw holes. Since the aim is to maintain continuous metal-to-metal contact the screw holes should be closely spaced. Each time the back plate is tightened down and subsequently removed, the solder gasket should be replaced. A design for the back plate is shown in Fig. 3.14. A waveguide for the aperture by which

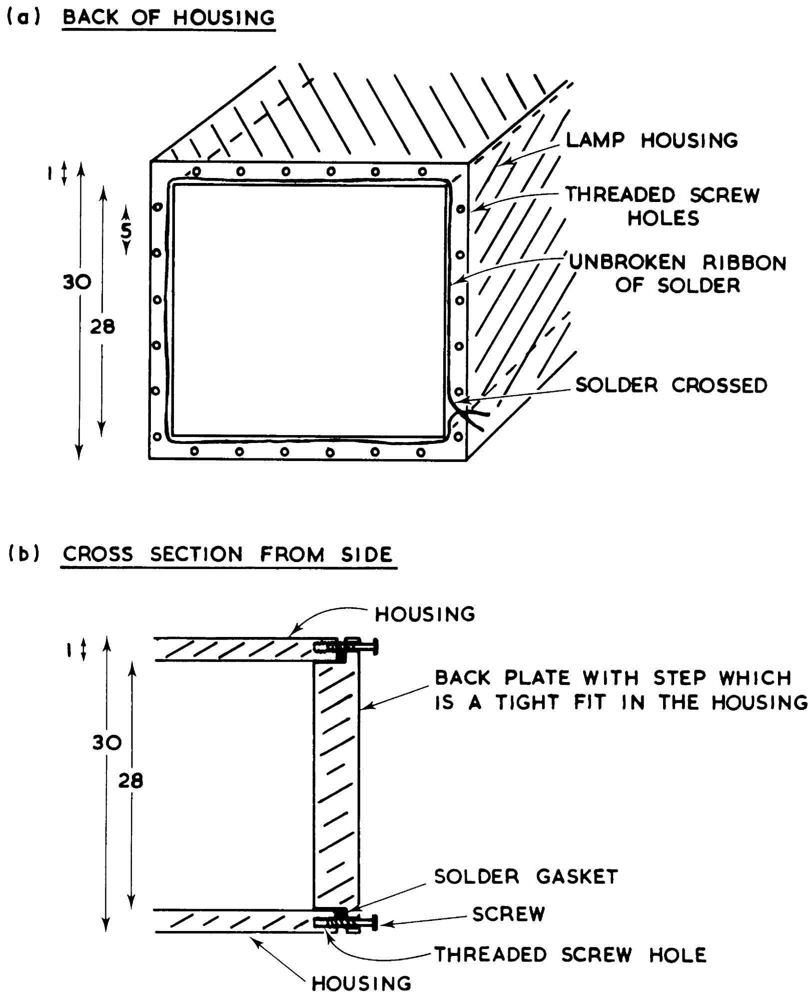


*Figure 3.14* Stepped backplate for lamp housing (not drawn to scale). Dimensions (in cm) are intended only as rough guide.

light exits to the sample is relatively easy to fit and can be threaded to accommodate a lens holder. Again a lip on the tube makes insertion of a solder gasket easy, as illustrated in Fig. 3.15. A shutter or iris diaphragm can also be accommodated in the waveguide but the mechanism should be so designed that only a small hole is necessary for the control lever. Some high voltage and BNC bulkhead connectors are of design similar to that of the waveguide and can be used with a solder gasket.

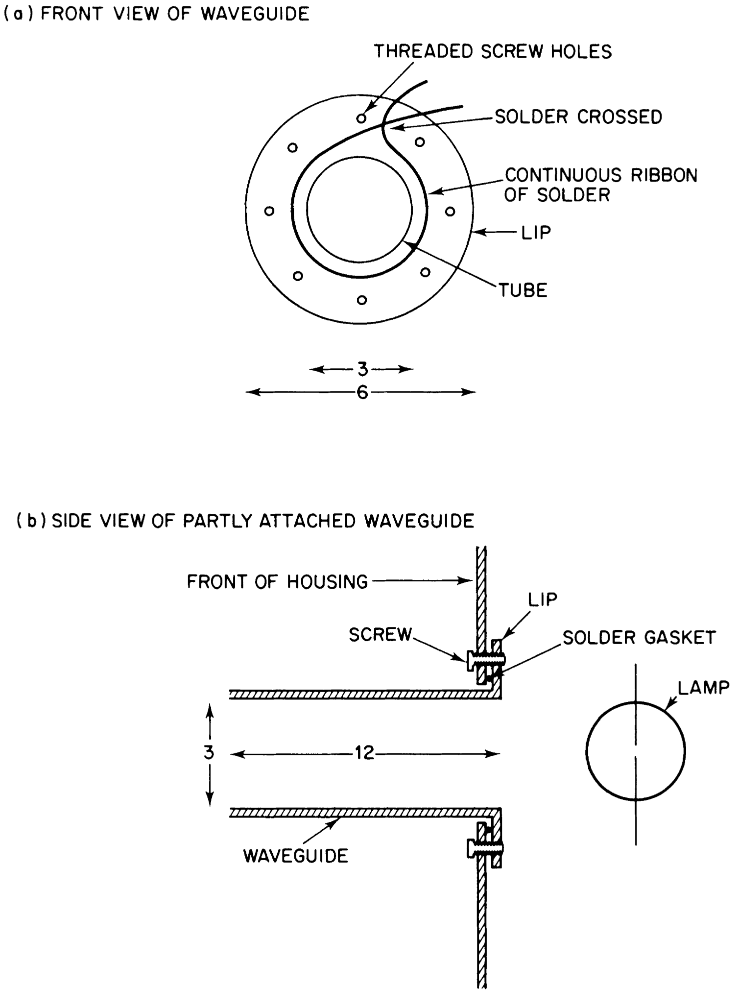


*Figure 3.15* Illustration of waveguide for r.f. filtering on housing light aperture (not drawn to scale). Dimensions (in cm) are intended only as a rough guide.

Since r.f. may also be generated in the high voltage power supply and be transferred along the high voltage cable into the housing, it may also be necessary to filter this voltage. A four stage $\pi$-type RC filter suitable for this purpose has been suggested by Lyke and Ware (1977). This filter should, of course, be accommodated in a shielded box which is attached to the lamp housing in such a way as to introduce no new ports for r.f. leakage. If the lamp is gated the thyratron heater voltage can be filtered by an LC filter of the type illustrated in Fig. 3.16. The small inductance, created by a number of coils of conductor wound round a reasonably high resistor, blocks r.f. signals but not the 50 or 60 cycles of the a.c. signal. The capacitors in the filter will pass r.f. but not the 60 cycle signal. They should be physically small so that they do not act as pick-up points.

For the transmission of signals from the trigger source and fluorescence PM to the electronics doubly-screened coaxial cable is recommended. If it is not available singly-screened cable may be further screened by drawing the braid from a larger diameter cable over the coaxial cable and clamping it tightly at the connectors. Lyke and Ware (1977) recommend passage of the cable carrying the trigger signal to a pulse transformer in a screened box in order to eliminate ground loops and r.f. carried along the cable skin. The transformer consists of two turns of No. 50 wire for both input and output in a 3.18 mm ferrite core.

It should be emphasized that with many types of lamp r.f. interference will not be severe and the foregoing precautions will not be necessary. If r.f. generation is suspected an antenna connected to an oscilloscope may help to trace the source. Occasionally interference originating in some equipment unconnected with the SPC instrument may be present. Because it is a regular

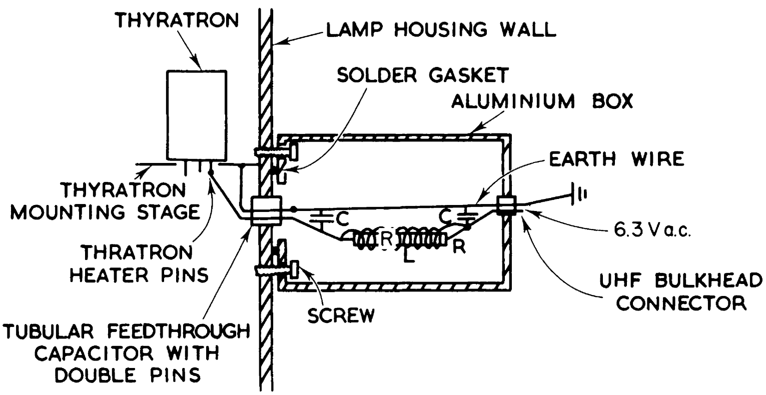


*Figure 3.16* Schematic diagram of $\pi$-type r.f. filter for thyratron heater voltage (not drawn to scale). L, inductance; R, resistor (47 k$\Omega$); C, capacitors (0.0015 $\mu$F).

signal with an interpulse spacing in the nanosecond time range it will also distort the data if picked up in the electronics. It may not be possible to filter this signal at source. In this case more elaborate screening procedures may be necessary. If adoption of doubly-screened coaxial cable for all intercomponent connections and slight raising of discriminator levels (see Section 5.3) does not eliminate the interference, specialized advice should be sought.

## 3.4 Pulsed Lasers

### 3.4.1 Introduction

Since the early 1970s, lasers, and in particular synchronously pumped dye lasers, have found increasing application in SPC experiments. The ways in which lasers can provide excitation pulses are numerous; however, in the following sections we shall deal only with the most commonly used laser sources. We have omitted discussion of nitrogen laser pumped dye lasers (Imasaka *et al.*, 1981) since at the present stage of development the nitrogen laser does not provide a high repetition rate, is relatively unstable, and frequently has extreme r.f. noise generation associated with its operation. Solid state and excimer lasers are again of low repetition rate and have not found wide applicability in SPC measurements and will also be excluded from the discussion. We shall concentrate almost exclusively on $Ar^+$ ion laser pumped dye lasers. Recently the $Kr^+$ ion laser has been developed to replace the $Ar^+$ ion laser in certain wavelength regions. At the time of writing it is too early to comment on its performance in the SPC instrument, but we expect that there will be very little difference between $Ar^+$ and $Kr^+$ ion lasers as regards general effectiveness of operation. The cavity length in reasonably sized ion lasers is such that the mode-locked pulse train has an interpulse separation of only a few nanoseconds, rendering it rather unsuitable for nanosecond lifetime measurements (but see Wild *et al.*, 1977; Spears and Hoffland, 1977). Similar remarks apply to the mode-locked train from a synchronously pumped dye laser, although such a laser can also serve for excitation of very short-lived samples (Kinoshita *et al.*, 1981). Consequently we confine our attention to laser systems in which the rate at which pulses are obtained from the laser is determined either by intra-cavity cavity-dumping or extra-cavity pulse selection with a Pockels cell.

### 3.4.2 Cavity-dumping in CW lasers

Pulses, at repetition frequencies suitable for SPC measurements, can be obtained from lasers operating CW if an acousto-optic modulator (cavity-dumper) is incorporated in the cavity (Roberts *et al.*, 1980; Rumbles *et al.*, 1982). In cavity-dumping the partially transmissive output mirror of the laser is replaced by a quartz plate placed at the focus of a high reflection antistigmatically compensated folded cavity, as illustrated in Fig. 3.17. To a non-optical face of the plate is attached a piezoelectric transducer which converts a pulsed r.f. signal into an acoustic wave propagating across the plate. This quartz plate now functions as a Bragg diffraction cell. The propagating acoustic wave causes regions of compression and rarefaction and, hence, periodic fluctuations in the index of refraction. In this way intra-cavity laser light is periodically deflected from its normal path and can be switched as pulses out of the cavity at repetition rates of from single shot to 5 MHz or greater.

The width of the output pulses is determined by the duration of the acoustic pulse and the fractional diffraction efficiency of the Bragg cell (Johnson, 1973). Pulse widths of 10 ns in SPC instruments have been reported (Roberts *et al.*, 1980). Peak power per pulse also depends on the diffraction efficiency and may in theory be as high as 50 times the average output power of the laser (Maydan, 1970). As a rough guide to the intensities obtainable in practice, a peak power of 20 W is reported for the cavity-dumped pulses from a 4 W $Ar^+$ ion laser (Rumbles *et al.*, 1982) while peak powers of 10 W have been obtained from the cavity-dumped output of a Rhodamine 6G dye laser pumped CW by this ion laser (Roberts, 1980). Cavity-dumped pulses have in general a highly reproducible interpulse separation (better than 1 part in $10^5$) and a repetition rate that is easily varied over a wide range.

In older generation commercial cavity-dumpers reflection of the acoustic wave from a second face of the Bragg cell led to a secondary peak in the tail of the primary pulse. However, this peak, though sometimes fairly large (*c.* 5%

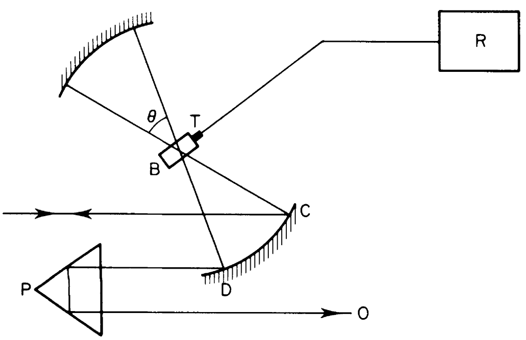


*Figure 3.17* Schematic outline of accousto-optic cavity-dumping. A, input and returned beams; B, Bragg cell; O, output beam; P, prism; R, r.f. driver; T, piezoelectric transducer.

of the primary), is a true optical pump and is found not to interfere with deconvolution. In recent models it has been eliminated and interpulse optical noise is negligible. A potential source of distortion in SPC data is the modulation in the carrier wave for the r.f. pulse in the cavity-dumper. If the acoustic frequency is large a smooth optical pulse is obtained (Maydan, 1970), but if it is low enough to be resolvable by the SPC detection system the optical pulse observed will be modulated by a frequency twice that of the acoustic carrier wave. This modulation has been observed in SPC instrument response functions (Spears *et al.*, 1978) and decay curves (Roberts, 1980) and can distort data reduction. However, it can be eliminated by slight adjustments in the Bragg cell orientation.

The cavity-dumped CW laser is easy to operate and furnishes stable high intensity pulses at MHz repetition rates. Since mode-locking is not involved mechanical stability in the laser table need not be perfect. With commercial ion lasers a reasonably sized cavity-dumper can fit in the existing laser cavity; in dye lasers however the cavity may have to be extended. A cavity-dumper that has found wide acceptance in SPC instruments is manufactured by Spectra Physics Inc*. A similar device is now marketed by Coherent Radiation Ltd*. Details regarding the construction, pulsing and operation of a home built cavity-dumper have been given by Spears and Larsen (1977).

Cavity-dumping from CW lasers suffers from the crucial drawback of producing relatively broad excitation pulses. Pulses generated in this way, even after frequency doubling, do not have FWHMs much shorter than 7 ns. Consequently, in spite of high stability, this type of pulse generation is not ideal for the measurement of picosecond decay times.

### 3.4.3 Cavity-dumping from mode-locked lasers

Laser mode-locking has long been employed as a means of producing narrow pulses of high peak power. In SPC applications a mode-locked ion laser with a cavity-dumper selecting a fraction of the mode-locked pulses can furnish an effective excitation source (Roberts *et al.*, 1980). A dye laser pumped CW by an ion laser may also be mode-locked (Spears and Cramer, 1978). In either method good pulse amplitude stability may be achieved by synchronizing the acoustic pulses in cavity-dumper and mode-locker (Spears and Cramer, 1978).

Among the methods by which mode-locking may be achieved (Smith, 1970), the most common in SPC sources is loss modulation through acousto-optic Bragg diffraction. In this method the loss is modulated at a frequency of $c/2l$ where $c$ is the velocity of light and $l$ is the length of the cavity resonator.

*See Appendix 3.A1.

Stable mode-locking therefore depends on an exact match between this frequency and the cavity length. Variations in cavity length arising from vibrations and temperature fluctuations must be avoided, preferably through operation of the laser in a constant temperature environment on a pneumatically stabilized vibration-free table.

Mode-locked lasers usually have average output powers 25% to 35% of the average power that results from CW operation. Pulse widths are in the range 100–200 ps. For the dyes Rhodamine B, 6G and 110 at a dump rate of 5 MHz Spears and Cramer achieved average power in the mode-locked pulses of between 25 and 100 mW. These powers are much greater than output powers from flash lamps (see Section 3.3.4) and combined with the narrow pulse width render lasers operated in this way a very attractive excitation source. Pulse widths narrower by more than an order of magnitude may be achieved, however, in synchronously pumped dye lasers.

### 3.4.4 Synchronously pumped mode-locked dye lasers

If the dye laser cavity is extended so that its length matches to within $2 \times 10^{-6}$ m the cavity length of the pumping mode-locked ion laser, the dye laser is said to be synchronously pumped (Harris *et al.*, 1977). A diagram of a synchronously pumped dye laser functioning as an SPC excitation source is given in Fig. 3.18. In this configuration the dye laser intermode spacing is an integral multiple of the mode-locker frequency and the dye jet is pumped synchronously by an ion laser pulse and a circulating dye laser pulse. Synchronous pumping yields output dye laser pulses of a few picoseconds duration (Chan and Sari, 1974) as illustrated by the autocorrelation trace in Fig. 3.19.

As in mode-locked ion lasers, the pulse separation in synchronously pumped dye lasers is determined by the length of the ion laser cavity and is usually about 10–15 ns. In one of the commercial synchronously pumped laser systems (Spectra Physics Model 171) the $Ar^+$ ion laser is mode-locked on the 514.5 nm line at an acoustic modulation frequency of about 41 MHz yielding output pulses at 82 MHz, pulse separation 12.2 ns. The average power of these pulses, the FWHM of which is about 150 ps, is 800 mW compared to 1.6 W for CW operation. This high power is desirable if the $Ar^+$ ion u.v. lines are to be mode-locked. It should be mentioned that it is difficult to introduce enough loss into the cavity to mode-lock the strong 488 nm $Ar^+$ ion line, although mode-locking of all the visible $Ar^+$ ion lines in an SPC excitation source has been achieved (Kinoshita *et al.*, 1981). In the commercial system referred to, dye laser pulses are output with a cavity-dumper usually operating at 4 MHz. Typical average powers at the wavelength of maximum intensity, 596 nm, are 60 mW. Although powers as high as 250 mW

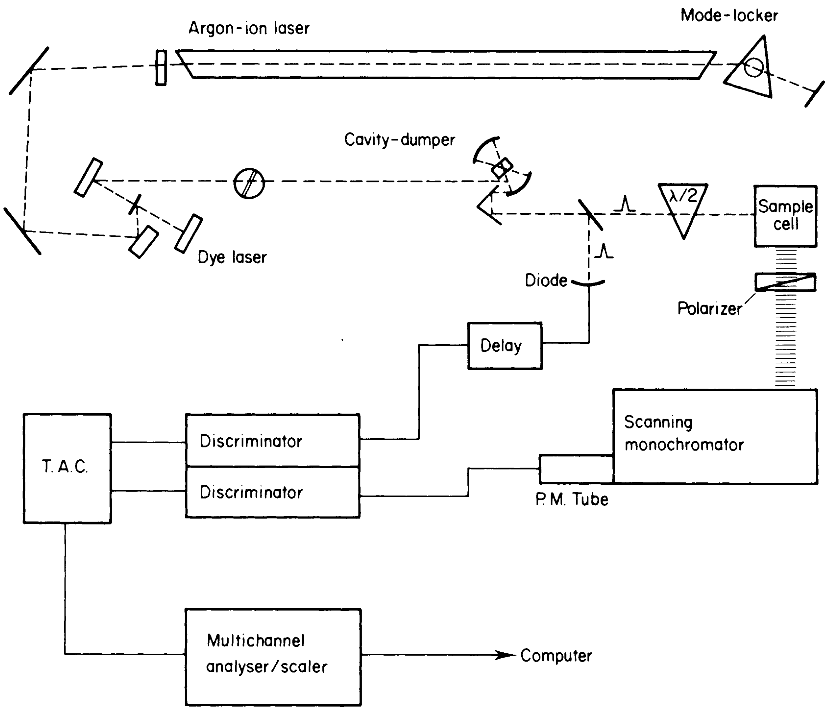


*Figure 3.18* Synchronously pumped system configuration.

in cavity-dumped pulses have been reported (Bushaw *et al.*, 1978), in routine operation the power is more likely to be in the range 50–100 mW. Typical average powers for non-cavity-dumped operation are about 250 mW (Robbins *et al.*, 1980). It should be noted, however, that extra-cavity pulse selection, in which the unused laser power is lost, is a less efficient process than cavity-dumping.

In commercial synchronously pumped dye laser systems pulse stability is excellent over a few hours operation, although mechanical drift in the cavity-dumper optics and bubbles in the dye jet may cause some pulse jitter with consequent rising edge deconvolution problems. This jitter can be monitored by deflecting a small amount of the output beam into a photodiode and observing the pulse shape on an oscilloscope. For this purpose, since it is changes in pulse shape that are important, the diode and oscilliscope need not have exceptionally fast rise times. Jitter that cannot be eliminated by adjustment of the optics may have its source in fluctuating non-uniformity in the dye jet. Crystallized dye particles can accummulate on the nozzle and should be removed. Air bubbles in the jet can cause intermittent loss of mode-

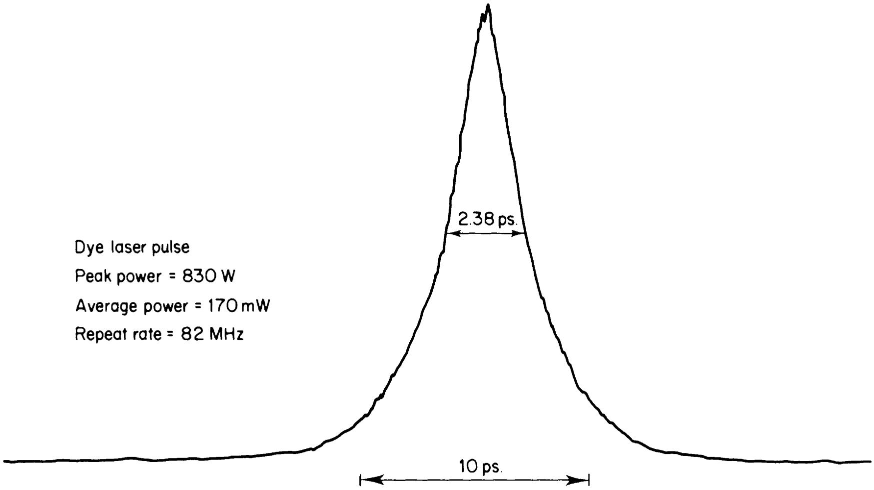


*Figure 3.19* The autocorrelation function of pulses obtained from a cavity-dumped synchronously pumped mode-locked dye laser. From this function the pulse width is deduced to be 6 ps. The synchronously pumped system was Spectra Physics Model 171/375/342.

locking and thus affect the pulse stability. If careful attention to the dye pressure fails to remove them a special filter may have to be employed. Vibrations, transmitted along the connecting tubing from the dye pump to the jet, can also cause instability. They can be effectively removed by passage of the dye solution through a simple glass trap of the type illustrated in Fig. 3.20. It has also been reported that an electronic feedback mechanism from a photodiode in the cavity-dumper to the ion laser mode locker driver enhances pulse stabilities considerably (Haugen and Lytle, 1979; Yamazaki, 1982).

Temperature control of the laser environment is important, not only as an influence on mechanical stability, but also as a guard against mode-locker malfunction. If the dissipation of heat by the laser raises the room temperature too much the temperature stabilizer on the mode-locker oven will be unable to maintain control and mode-locking will be interrupted. The laser optics should be screened from airborne dust particles since the beam can burn such particles permanently on to optical surfaces. In many laboratories shoes for use only in the laser room are standard. If a dust remover is not fitted a gentle flow of nitrogen over the mode-locker (and cavity-dumper) crystal should prevent formation of inhomogeneities. Care must be taken to keep the nitrogen flow very low; otherwise instabilities in the ion laser pulses will result.

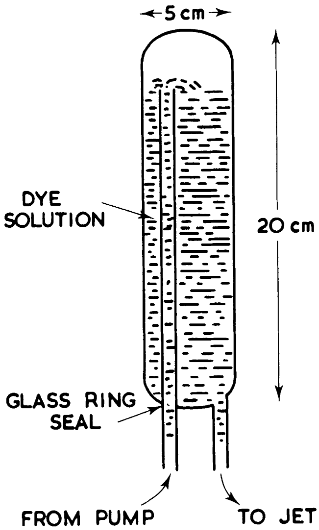


*Figure 3.20* Glass trap for damping vibrations transmitted from dye pump.

### 3.4.5 Pulse selection with a Pockels cell

In the preceding section we have assumed that pulses leave the laser cavity at a repetition rate suitable for nanosecond lifetime measurements. The main disadvantage of selecting pulses in this way is the cost of commercial cavity-dumpers. Costs can be considerably reduced by selecting pulses from the mode-locked train with an extra-cavity Pockels cell shutter.

A Pockels cell is a device which, when subjected to a suitable applied voltage, behaves like a birefringent crystal. The birefringence is directly proportional to the applied voltage for a Pockels cell. When the voltage is zero the cell is not birefringent. The shutter consists of crossed polarizers and a Pockels cell such that upon suitable application of a voltage, of the order of 1–5 kV, to the Pockels cell, the laser pulse is transmitted. Pockels cells can be triggered simply by use of avalanche diodes, at some cost in terms of disturbance to detection electronics by resulting bursts of r.f. (Ware *et al.*, 1983).

SPC experiments with a Nd:YAG laser have also been performed by means of a Pockels cell (Sadkowski, 1981). Since the Pockels cell driver delivers relatively high r.f. powers very much more careful attention must be paid to electrical screening than is necessary with cavity-dumpers. The other main disadvantage of the technique in comparison with cavity-dumping is the relatively low repetition rate that can in practice be attained ($\leqslant 100$ kHz).

### 3.4.6 Wavelength selection

Lack of easy tunability over a wide wavelength range is the major disadvantage, apart from cost, associated with laser based excitation sources compared to flash lamps. Nevertheless, as is illustrated in Fig. 3.21 a wavelength range from 415 nm to 710 nm is available with a single $Ar^+$ ion laser–dye laser system. With frequency doubling (*vide infra*) a wide range of wavelengths can be produced.

As can be seen in Fig. 3.21 the dye Rhodamine 6G alone, gives access to the wavelength range from 560 to 650 nm, which is ideally suited for lifetime studies of compounds of interest in solar energy research such as porphyrins. When light at these wavelengths is frequency doubled naphthalenic compounds can be readily excited. In addition, owing to the high intensities available, anthracene and its derivatives can also be studied. In Fig. 3.22 is shown the decay curve of anthracene at $2 \times 10^{-5}$ M in cyclohexane excited with frequency-doubled light at 300 nm from a Rhodamine 6G synchronously pumped dye laser. In spite of the window in the anthracene absorption at this wavelength the decay curve was collected in a matter of seconds and was deconvolved very successfully. Tryptophan, indole and many biological fluorescence probes are also amenable to study in the wavelength region from 280 to 325 nm, while benzene and its derivatives can be excited by the frequency-doubled $Ar^+$ ion lines.

With reasonable foresight in planning an experimental programme a change in the dye laser solution should not interrupt research, although a day or two will probably be given to attaining good mode-locked lasing with a new dye. It should be noted that in Fig. 3.21 the $y$-axis is logarithmic. Therefore considerably reduced output powers should be expected for dyes other than Sodium Fluorescein and the Rhodamines. Nevertheless, provided that the necessary optics and frequency-doubling crystals are available,

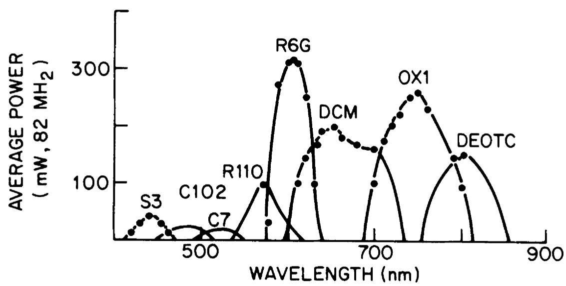


*Figure 3.21* Wavelength range available with an $Ar^+$ ion laser–dye laser combination (from Spectra Physics).

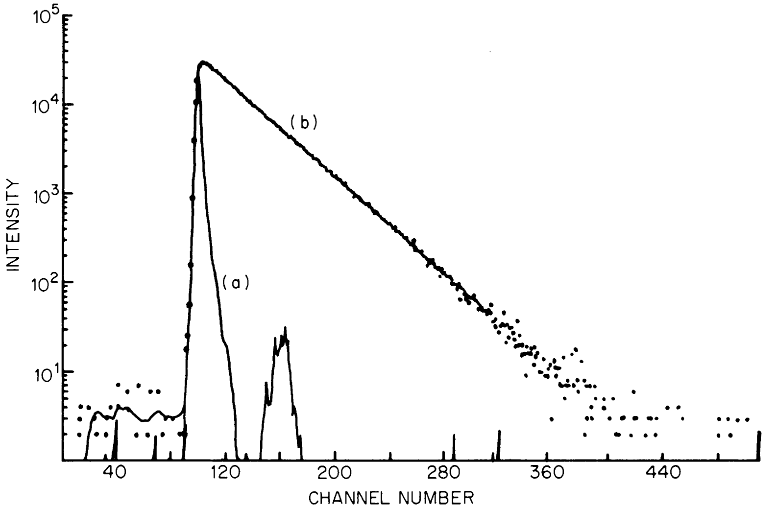


*Figure 3.22* Decay of anthracene ($2 \times 10^{-5}$ M) in cyclohexane following laser excitation at 300 nm. (a) Instrument response function; (b) points, observed decay; line, fitted curve. 0.164 ns per channel, $\tau = 5.23$ ns $\chi_\nu^2 = 1.04$ DW = 1.84 (see Section 6.7).

intensities should be adequate for most experiments where excitation is in the range 225 to 700 nm.

(We should point out that the element for wavelength tuning in commercial dye lasers cannot be easily fitted with a scanning mechanism. It is to be hoped that the manufacturers will re-design this element in the near future.)

## 3.4.7 Second harmonic generation

The efficiency of frequency doubling (SHG) in a non-linear crystal is proportional to the square of the peak power of the undoubled pulses. This dependency (Franken and Ward, 1963) is given by the simplified equation:

$$P_S = \frac{JP_I^2 l^2 d^2 \sin^2\theta}{w_0^2} \frac{\sin\left(\frac{\Delta kl}{2}\right)^2}{(\Delta kl/2)} \tag{3.2}$$

in which $J$ is a constant, $P_I$ is the peak power of the incident pulse assumed to be a single mode Gaussian, $l$ is the crystal length, $d$ the SHG coefficient, $w_0$ the minimum beam waist, $\theta$ the angle between the crystal optic axis and the direction of the incident beam under phase matching conditions and $\Delta kl$ is the phase mismatch between the fundamental and second harmonic frequencies. One consequence of this property of non-linear crystals is that the pulse width is shortened upon frequency doubling. To take an example already referred to, the cavity-dumped (Spectra Physics Model 166) output pulses at 596 nm of a CW dye laser have a width of 10 ns at half maximum compared to 7 ns for the frequency-doubled pulses at 298 nm.

Because of the power squared dependence, frequency doubling is an inefficient process for pulses of the powers encountered in mode-locked lasers operated at high repetition rates. As a typical example, when the cavity-dumped output beam of a synchronously pumped dye laser at 608 nm, repetition rate 4 MHz and average power 20 mW ($1.5 \times 10^{10}$ photons per pulse) was frequency doubled in an angle tuned ADP crystal, temperature stabilized at 35°C, the intensity of the u.v. pulses, as determined by ferrioxalate actinometry, was $5 \times 10^6$ photons per pulse (Phillips and O'Connor, 1981). This figure represents an efficiency of less than 0.1%. With some extra effort higher efficiencies may certainly be attained (Robbins *et al.*, 1980; Bushaw *et al.*, 1978) but for routine SPC operation powers at the sample in excess of 1 mW should not be expected. Even with much lower frequency conversion efficiencies u.v. operation of pulsed lasers offer a considerable improvement on conventional flash lamps (see following section).

In Table 3.3 we have listed a number of SHG crystals together with the

*Table 3.3* Some frequency doubling crystals.

| Symbol[a] | Tuning range of fundamental/nm | Comments |
|---|---|---|
| ADP | 510–550 | temperature tuned |
| AD*P | 515–555 | temperature tuned |
| ADA | 565–520 | temperature tuned |
| RDP | 615–630 | temperature tuned |
| RD*P | 632–650 | temperature tuned |
| RDA | 690–700 | temperature tuned |
| CD*A | 1040–1060 | temperature tuned |
| CDA | 1060–1070 | temperature tuned |
| KPB | 434–510 | angle tuned |
| KDP | (518–940) | angle tuned range in region 518–940 nm depends on cut |
| ADP | 600–720 | angle tuned |

[a]ADP : ammonium dihydrogen phosphate;
AD*P : ammonium dideuterium phosphate;
KDP : potassium dihydrogen phosphate;
ADA : ammonium dihydrogen arsenate;
RDP : rubidium dihydrogen phosphate;
CDA : caesium dihydrogen arsenate;
KPB : potassium pentaborate;
etc.

wavelength range of the fundamental frequency. In general a crystal with a 45°Z cut (90° phase matching) is suitable for temperature tuning. More convenient to use however are angle tuned crystals for which a different cut yields a different tuning range.

### 3.4.8 Trigger pulse

For lasers, as for gated flash lamps, it is preferable to derive the TAC trigger pulse from a photomultiplier or diode viewing the pulses directly rather than from the electronics in the mode-locker, cavity-dumper, or Pockels cell driver. The diode may be placed behind the sample cell or in a position viewing a small deflection from the exciting laser beam.

## 3.5 Summary of Flash Lamps and Pulsed Lasers

In this section the relative advantages and disadvantages of pulsed laser and flash lamp excitation sources in SPC experiments will be briefly summarized under a few important headings. While storage ring radiation must be regarded as a somewhat special case, outside the convenient availability of most research workers, its properties will be mentioned in the appropriate sections.

### 3.5.1 Intensity

In general the intensity of the fundamental frequency from all the laser systems discussed in this chapter is orders of magnitude higher than radiation generated in flash lamps. Even an average output power from a dye laser as low as 20 mW at 600 nm represents $6 \times 10^{16}$ photons per second, vastly in excess of the intensities available from flash lamps. In the u.v., where most of the output power of flash lamps is concentrated and where inefficient frequency doubling reduces laser powers by two orders of magnitude or more, closer scrutiny is necessary. From Table 3.2 it can be seen that deuterium- and air-filled flash lamps deliver typically, $3.3 \times 10^{13}$ and $3.5 \times 10^{14}$ photons per second, respectively, into a wide wavelength range and a solid angle of $4\pi$ steradians. If it is assumed that a lens can collect radiation emitted into 0.3 steradians and that losses in a monochromator amount to only 90%, the number of photons incident on the sample per second will be about $7 \times 10^{10}$ and $8 \times 10^{11}$ for deuterium and air, respectively. These intensities are still much lower than the $2 \times 10^{13}$ photons per second available from the synchronously pumped dye laser referred to in Section 3.4.7. Even if wavelength is selected with an interference filter, air lamp intensities in a fairly narrow spectral band do not match those available from lasers. For the ACO storage ring facility at Orsay the intensity at the sample is calculated to be 6 $\times 10^{11}$ photons $s^{-1}$ $nm^{-1}$ at 300 nm (Lopez-Delgado *et al.*, 1974). If the experimental intensity is similar, the storage ring source compares favourably with air flash lamps but lacks the power of the laser.

## 3.5.2 Data collection time

The time required to collect a decay curve to a given precision is closely related, of course, to the intensity of the excitation source. An additional factor is the flash repetition rate, higher rates leading to more efficient TAC operation and shorter collection times. It is this factor, as much as their higher intensities, that makes measurement times with cavity-dumped lasers so short. The advantage is lost when pulses are selected with a Pockels cell, which is usually operated at $< 100$ kHz. Typical collection times with 4 MHz laser excitation are 0.5 to 1 minute for a decay curve with 30 000 counts in the channel of maximum counts. Storage ring sources also operate at MHz repetition rates.

It should be noted that as the decay time of the samples under investigation gets longer the repetition rate of the cavity-dumper will have to be lowered in order to allow the fluorescence resulting from one flash to decay before the next excitation event, and so prevent miscorrelation in the TAC. Some loss in overall intensity usually accompanies lower dumping rates. However, for most nanosecond lifetime measurements a repetition rate of 800 kHz (1250 ns interpulse separation) will be sufficiently low. Flash lamps are capable of operating at a maximum of only 150 kHz and in routine operation are rarely driven above 100 kHz. Storage ring radiation and cavity-dumped lasers are therefore more efficient than flash lamps and relatively low repetition rate lasers (Pockels cell pulse selection) in time-correlated nanosecond decay time measurements.

## 3.5.3 Wavelength selection

Wide spectral continua are generated in high pressure lamps filled with nitrogen, deuterium and hydrogen. In the more common low pressure lamps the pressure broadened nitrogen continuum is lost and only a limited number of wavelengths is available. Deuterium- and hydrogen-filled low pressure lamps do furnish broad continua but at reduced intensity compared to nitrogen or air (Table 3.2). Dye lasers, while not yet developed to the stage where wavelength tuning over wide ranges can be performed automatically, are tunable with a single dye over 50 nm and concentrate all the intensity in an extremely narrow wavelength band. For this reason a laser source is probably the only reliable means of excitation in single vibronic level studies. With a certain amount of planning, experiments requiring excitation over a range of a few hundred nanometres can be performed with an ion laser–dye laser combination. It is still true to say, however, that for excitation wavelength scanning over a wide range a flash lamp is necessary. If this type of excitation is required the relatively low intensities provided by deuterium lamps (if the more common low pressure lamp is chosen) will have to be tolerated. The radiation from a storage ring is a broad continuum (Fig. 3.1) which can be easily scanned by means of a monochromator.

### 3.5.4 Spectral resolution of emission

The extent to which the spectral bandwidth of the fluorescence can be narrowed is directly dependent on the intensity of the excitation source. For this reason in SPC instruments with laser excitation sources a high emission monochromaticity can be attained. If optical systems in flash lamp instruments are carefully designed, monochromators can be placed in both excitation and emission light paths.

### 3.5.5 Pulse width

Flash lamp pulse widths are of the order of 0.5 ns. Synchronously pumped mode-locked dye lasers furnish pulses with typical widths less than 10 ps. The advantage of this type of laser is obvious. Mode-locked ion laser pulses have widths of 100–200 ps whereas cavity-dumping from a CW laser furnishes 10 ns pulses. Pulses of 3 ns can be obtained from a Pockels cell in conjunction with a CW laser. If very short decay times are to be measured the mode-locked laser is clearly preferable, especially in the light of recent advances in reducing detector response times (see Section 4.5). Pulse widths in storage ring sources vary considerably from one installation to another, but are generally in the range 100 ps–1 ns.

### 3.5.6 Pulse stability

We have emphasized that accuracy in lifetime measurements depends to a large extent on pulse-to-pulse reproducibility. If pulse stability is perfect the pulse width imposes no limitation on the time resolution of the experiment. However, no source is perfectly stable and pulse jitter, which is usually proportional to pulse width, will be smaller in absolute terms in a narrow pulse. There is no doubt that all excitation sources have periods of instability. Most of the "rising edge effects" that hinder successful deconvolution over the entire decay curve (see Chapter 6) probably have their origin in excitation pulse jitter.

Acceptable stability is difficult to attain in air-filled lamps owing to electrode corrosion by the discharge. Similarly a great deal of attention is required initially in order to obtain stable operation of mode-locked lasers. CW lasers, on the other hand, from which pulses are selected by means of a cavity-dumper, provide extremely reproducible pulses without a great deal of effort on the part of the operator. Deuterium, hydrogen or nitrogen are less difficult flash lamp gases than air to work with but are subject to intermittent instability effects.

It appears, therefore, that at the present stage of development neither flash lamps nor mode-locked lasers can be guaranteed to provide, without some effort, excitation sources of acceptable stability. It should be emphasized, however, that operating conditions for all sources can be found such that stable excitation pulses (as judged by the absence of rising edge effects in deconvolution) are provided over relatively long (hours) times. Long-term drift is probably ineradicable, so that shorter data acquisition times are preferable.

### 3.5.7 Instrument response function

There is thought to be little change in the pulse shape from hydrogen- or deuterium-filled flash lamps over the wavelength range 200 to 450 nm. While this belief has not as yet received direct experimental support, it is justified by the success in deconvolution (at least over the decaying portion of the decay curve) achieved with instrument response functions collected at the emission wavelength. However, some contribution to rising edge distortions may originate in a slight wavelength dependence of the pulse shape. Until it is regular practice to use the entire decay curve in the deconvolution procedure, no definite conclusion can be reached. Our reluctance to accept the hypothesis of unchanging pulse shape stems in part from the high likelihood of some air contamination of hydrogen- or deuterium-filled flash lamps. Pulse shape is known to change from one spectral line to another in the nitrogen $C^3\pi u \rightarrow B^3\pi g$ transition. Similarly, for laser sources the instrument response function must be recorded at the excitation wavelength. The pulse shape in storage ring sources is believed to be constant over a wide wavelength range.

It will be clear that as far as the correct determination of the true instrument response function is concerned deuterium- or hydrogen-filled flash lamps appear to have the advantage over pulsed lasers – an advantage that must be considered in conjunction with the measurements of and corrections for wavelength effects discussed in detail in Sections 2.3, 3.3.2(c), 4.4 and 6.3.

### 3.5.8 Polarization

Exciting radiation from laser and storage ring sources is completely polarized and is ideal for experiments designed to take advantage of polarization or depolarization of fluorescence. Light output from flash lamps has some but by no means complete polarization and is considerably attenuated upon passage through a polarizer.

### 3.5.9 Scattered light

Stray exciting light resulting from reflections in the sample cell will be greater for the more intense laser sources. On the other hand the laser beam is almost perfectly focussed in comparison to flash lamp radiation and can therefore be easily prevented, by means of baffles from reaching the detector directly. In addition, since the laser radiation is concentrated into a narrow spectral bandwidth it can be filtered much more effectively than flash lamp or storage ring scattered radiation.

### 3.5.10 Radio frequency noise generation

The amplitude of the r.f. pulses to cavity-dumpers and mode-lockers is not large enough to cause any pick-up effects in the detection electronics. Pockels cell drivers generate very powerful r.f. voltages from which the detection system must be screened carefully. Some flash lamps generate detectable r.f. signals while others are quite free of this source of distortion. If the manufacturers' specifications are to be believed, in commercial SPC instruments r.f. interference is absent.

### 3.5.11 Expense

The home built flash lamp is the least expensive excitation source: it can be constructed from materials available in most laboratories. Perhaps the most expensive part is the monochromator. Clearly, commercial flash lamps will cost more. Most costly are lasers, in particular synchronously pumped dye lasers. In addition to the cost of the laser (and mode-locker) it may be necessary to incur expenses for a cooling water supply, deionizer for cooling water, fast photodiode and oscilloscope, replacement ion laser tubes, optics and dyes for wavelength conversion, cavity-dumper, Pockels cell, service by the manufacturer, etc. Cavity-dumpers are very much more expensive than Pockels cells, but are probably preferable in all other respects in the SPC experiment.

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## Appendix 3.A1

### SPC instrument manufacturers

Applied Photophysics Limited, 20 Albemarle Street, London W1X 4BS, UK.

Low pressure gated flash lamp (capable of operation at 200 kHz). Glass-bodied lamp. PM tube: Philips XP2020Q. ORTEC electronics. Digital Corp PDPII microcomputer. Software capable of single, double and triple exponential analysis with automatic shift (analytic method) and scattered light correction, and option to analyse with fixed shift and lifetimes.

Edinburgh Instruments Limited, Riccarton, Currie, Edinburgh EH14 4AP, Scotland.

Low pressure gated lamp capable of operation at 150 kHz but optimized performance is at 25 kHz. Metal lamp of coaxial design. PM tube: Philips XP2020Q. ORTEC electronics. Lamp design illustrated in Fig. 3.11.

Photochemical Research Associates, Meg Drive, London, Ontario, Canada.

Low pressure gated flash lamp capable of operation at 60 kHz. Similar to the design in Fig. 3.10. Side on Hamamatsu PM. ORTEC electronics (but

ELSCINT snap-off timing single photon discriminator). PDP 11 microcomputer with software capable of single, double and triple exponential analysis.

Horiba Limited, Miyanohigashi Kisshoin, Minami-ku, Kyoto 601, Japan.

High pressure free-running flash lamp capable of operation at 20 kHz. Horiba electronics including multichannel TAC (see Section 5.2.5(c)). Computer includes two CPUs so that simultaneous data analysis and acquisition is possible.

## Synchronously pumped dye laser systems

*Spectra Physics (USA)*

Laser instruments Division, 1250 West Middlefield Road, Mountain View, CA 94042.
Tel. (415) 961 2550 TWX (910) 379 6941 Telex 348488

Albuquerque, NM
(505) 881 7577

Atlanta, GA
(800) 631 5693

Boston, MA
(800) 631 5693

Chicago, IL
(800) 323 0583
(312) 956 0882

Cleveland, OH
(800) 323 0583

Houston, TX
(800) 231 3567
[in Texas (713) 688 9886]

Los Angeles, CA
(714) 770 8545

Piscataway, NJ
(800) 631 5693
[in NJ (201) 981 0390]

Washington, DC
(301) 345 7333

*Worldwide*

Spectra Physics France, 3 rue Leon Blum, Zone Industrielle de Glaises, 91120 Palaiseau France.
Tel.: 33 6920 2500 Telex: (842) 691183

Spectra Physics GmbH, Siemensstrasse 20, D-6100 Darmstadt, West Germany.
Tel.: 06151 7080 Telex: (841) 419 471

Spectra Physics Limited, 17 Brick Knoll Park, St Albans, Herts, AL1 5UF, UK.
Tel.: (0727) 30131 Telex: (851) 23578

Spectra Physics B.V., Kanaaldijk Noord 61, 5642 Eindhoven, The Netherlands.
Tel.: 040 81 45 55 Telex: 51668

Spectra Physics AG, Schwiezergasse 39, 4056 Basel, Switzerland.
Tel.: 061 380075 Telex: 064335

*Canada, Latin America, Pacific Areas*

Spectra Physics International, 2905 Stender Way, Santa Clara, CA 95051, USA.
Tel.: (408) 249 5200 TWX: (910) 338 0220 Telex: 357 460

## Coherent Radiation (USA)

Coherent Laser Division, Corporate Headquarters, 3210 Porter Drive, Palo Alto, CA 94304.
Tel.: (415) 493 211 Telex: 34 8304

Coherent: Eastern USA, 1000 West 9th Avenue, Suite A, King of Prussia, PA 19406.
Tel.: (215) 337 3035 Telex: 84 6179

Coherent: Midwest USA, 870 East Higgins Road, Suite 142, Schaumburg, IL 60195.
Tel.: (312) 843 1650 Telex: 28 3592

*Worldwide*

Coherent limited, Science Park, Milton Road, Cambridge CB4 4BH, UK.
Tel.: 0223 68501 Telex: 817466

Coherent GmbH, Hermanstrasse 54-56, D 6078 Neu-Isenburg, West Germany.
Tel.: 06102 27073 77 Telex: 4 185656

Coherent SARL, 55 Rue Boussingault, 75013 Paris, France.
Tel.: 1 5898939 Telex: 842 204 900

Coherent BV, Meenthof 15, 1241 C.P. Kortenhoef, The Netherlands.
Tel.: 35 62504 Telex: 43514

Coherent Srl, Residenza Mestieri, Milano 2, 1 20090 Segrate, Italy.
Tel.: (02) 2138905 Telex: 843320