

Technical Report 002

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Designing a laser flash photolysis sample compartment

Laser flash photolysis can be performed using either front-face excitation, or 90-degree excitation, where the monitor and laser beams are perpendicular to each other. These notes concentrate on the latter, although a few comments on front-face excitation will be presented near the end.

Two parameters are important in determining the quality of the resulting signal: (i) the transient absorbance, and (ii) the intensity of the monitoring beam in the region of space where the monitoring light and laser beam overlap. These two parameters are closely linked in laser flash photolysis, and it is easy to improve on one while causing a deterioration of the other.

The transient absorbance, usually labeled as ΔOD , is in fact a “change in absorbance” since it uses as a reference the absorbance of the initial solution; as a result ΔOD values in laser flash photolysis can be positive, negative or zero. Negative values are obtained when the laser pulse “bleaches” or destroys an initially absorbing material. Thus, it can only occur at wavelengths where the initial sample has some absorbance. The absorbance of a transient is determined by Beer’s law, i.e.:

$$\Delta OD = \Delta \epsilon \times c \times l \quad (1)$$

Where $\Delta \epsilon$ is the extinction coefficient difference between the transient and its ground state precursor at the monitoring wavelength, l the optical path along the monitoring beam, and c

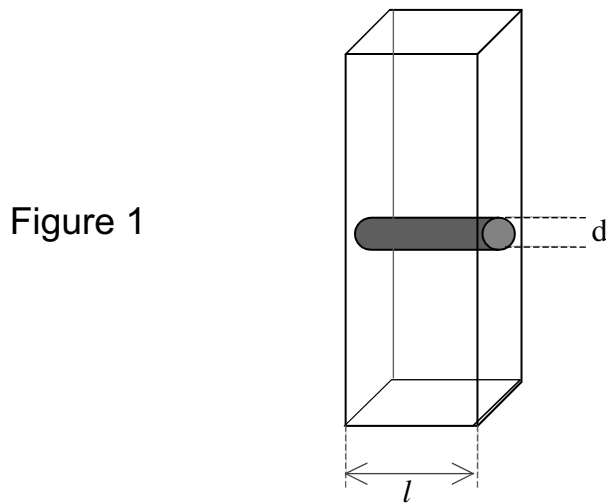
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the transient concentration. Usually one has little control on $\Delta\varepsilon$, other than choosing a monitoring wavelength near the absorption maximum. The optical path, l , is frequently determined by the experimental configuration, and changing it by more than a factor of 2-3 can be difficult. In Luzchem's mLFP systems the standard is $l = 1\text{cm}$, although other optional sample holders are available.

A typical laser flash photolysis sample may be 3 or 4 ml; however the monitored volume is only a small portion of the sample, generally a cylinder along the path of the sample cuvette as shown in Figure 1.



Thus, the monitored volume (V_m) is given by equation 2, where d is the diameter of the cylinder monitored.

$$V_m = l \times \pi \left(\frac{d}{2} \right)^2 \quad (2)$$

For example, for $l = 1\text{cm}$ and $d = 3\text{mm}$, V_m is only 71 microliters, representing only 2.4% of the volume for a 3 ml sample.

The concentration of transient generated in the volume V_m will be a function of the reaction characteristics (such as its quantum yield), the laser power, beam quality, beam alignment, and quite importantly, the absorbance of the sample at the laser wavelength. It is clear that very

low sample absorbance will lead to weak ΔOD values, since many of the laser beam photons will be transmitted, rather than absorbed. Something less obvious is the fact that high sample absorbance can also lead to weak signals, in addition to a myriad of other problems (*vide infra*). Therefore, which is the optimum sample absorbance at the laser wavelength?

Let's assume that the monitoring beam has a 3 mm diameter. A section of the cuvette, as viewed along the monitoring beam axis, will appear as in Figure 2.

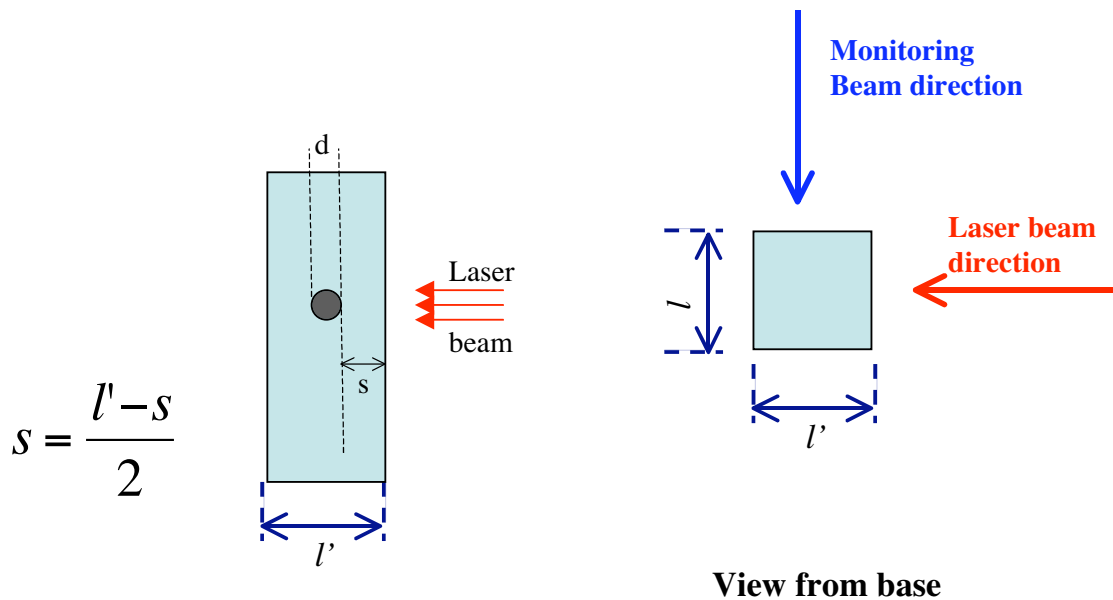


Figure 2: Laser and monitoring beam geometry

In our case we will assume a cuvette with square cross-section, or $l = l'$, and that the monitoring beam hole is centered in the cuvette. If d is 3 mm, and $l' = 1\text{cm}$, then $s = 3.5\text{mm}$. Thus, the laser light transmitted after transversing “ s ” (T_s) and after transversing “ s ” and “ d ” (T_d) will be given by (T stands for transmittance):

$$T_s = 10^{-s \times A} \quad (3)$$

$$T_d = 10^{-(s+d) \times A} \quad (4)$$

where A is the absorbance of the sample at the laser wavelength, for an optical path (l') of 1 cm. If we define the effectiveness, E , as the percent of laser light absorbed while transversing “ d ”, then

$$E = 100(Td - Ts) \quad (5)$$

Figure 3 shows plots of E vs. A for several values of “ d ”, always assumed centered in a 1 cm cuvette.

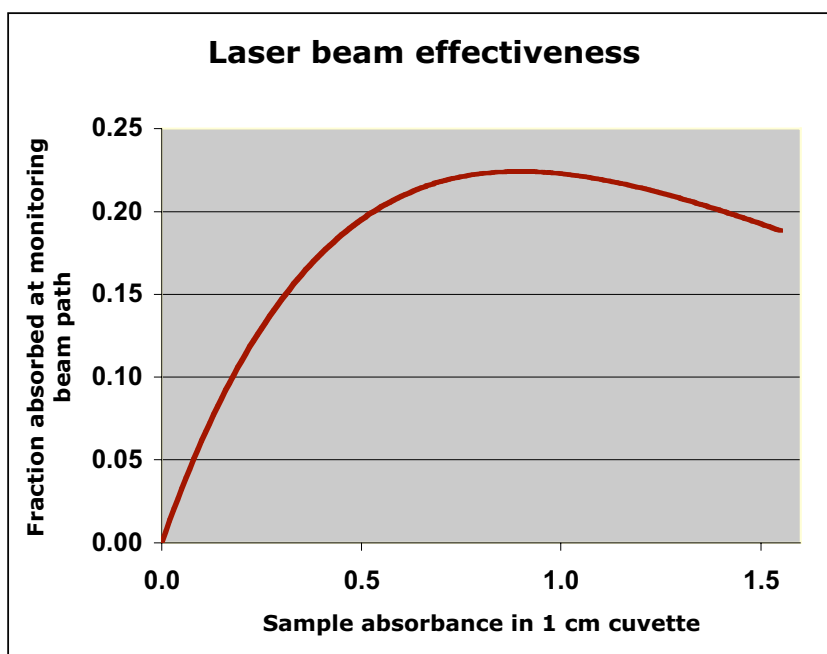


Figure 3: Laser pulse usage in the overlap region with the monitoring beam as a function of sample absorbance (at the laser wavelength) in a 1 cm cuvette.

Thus, in typical experimental set-ups the optimal absorbance would be around 0.8. However, little is gained for absorbances higher than 0.5. In general, lower absorbances have some advantages, specifically, (a) more homogeneous transient concentration; (b) less chance of inducing shock waves; and (c) better monitoring capabilities in the regions where the sample absorbs. Combining all these factors, recommended sample absorbance values at the laser wavelength are between 0.3 and 0.5 in the sample cuvette.

For practical purposes, in the discussion that follows we will assume a rectangular cross-section of the same area as the circular section of Figure 2. The details of the assumption are graphically shown in Figure 4.

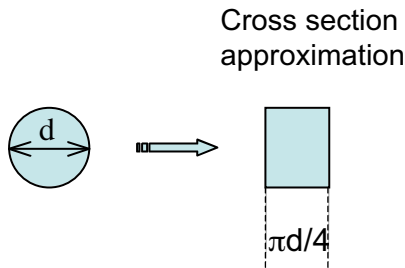


Figure 4: Equivalent cross sections

The I0 question: If we want to maximize the amount of monitoring light reaching our detection system (I_0), why not use a large value of “ d ”, thus maximizing light throughput through the cuvette and reducing in the process the value of “ s ”, the section of the cuvette where the absorbed laser light is not used to generate recordable signal?

We will now discuss different situations. In the first one the monitoring beam has been taken to the extreme of $d = 1$ cm while retaining the laser beam vertical size at 3 mm, and assuming that the laser beam fills completely the 1 cm optical path (l) of the monitoring beam, Figure 5.

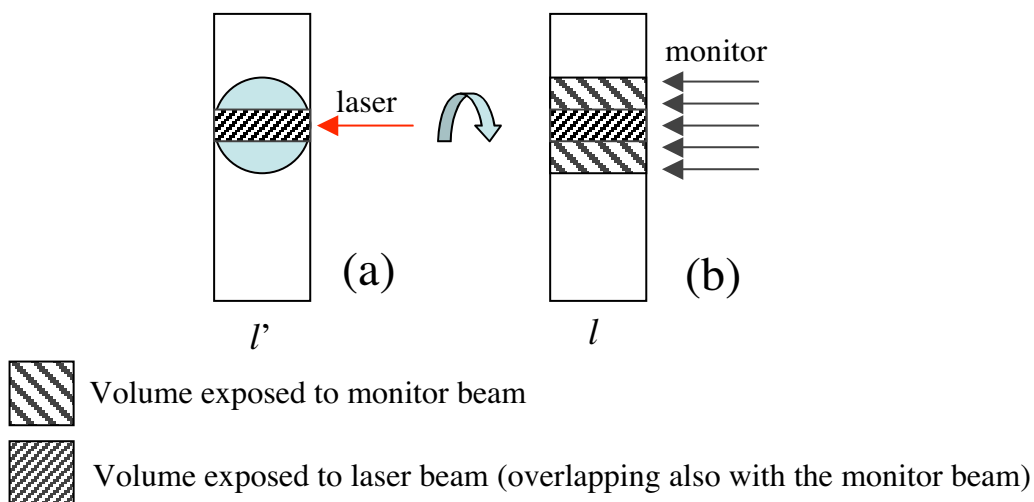


Figure 5: Overlap of monitor and laser beam for $d = 1$ cm

According to Figure 5a, the fraction of the monitoring beam carrying signal is approximately:

$$\text{effective fraction} = \frac{d \times l}{\pi \left(\frac{l}{2}\right)^2} = \frac{4 d}{\pi l} \quad (6)$$

which for $l = 1 \text{ cm}$ and $d = 3 \text{ mm}$ corresponds to about 38%. The result is even worse is one considers that most monochromators accept a vertical line (given by the slit) as light input. The practical result is artificially high I_0 values, artificially low ΔOD values, and non-linear behavior. Thus, claims of high I_0 values and ability to detect low ΔOD values should be taken with a grain of salt: they may simply reflect poor instrument design.

Let's now assume that the monitoring beam size is increased as in Figure 5, but that the vertical coverage of the laser beam is also increased so as to irradiate the value exposed to the monitoring beam. This is illustrated in Figure 6.

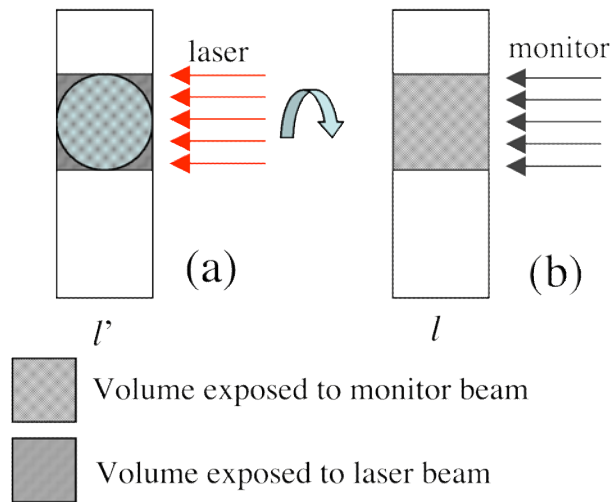


Figure 6: Full overlap of large laser and monitor beams, see text.

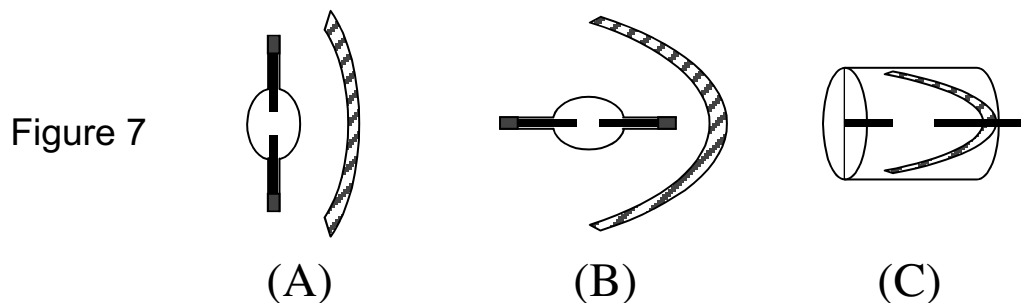
In this case, the effective fraction is 100%, but in order to achieve this the laser beam had to be expanded for 3 mm to 10 mm vertical dimension with a loss of 66% of the ΔOD relative to the alignment of Figure 2. This is due to the fact that the same number of photons lead to a lower transient concentration if the volume excited is larger. Note also that in the alignments of Figures 5 and 6 the transient concentration is very inhomogeneous. For example, for a

sample absorbance of 0.5 (at the laser wavelength) the ratio of concentrations “front/back” is ~ 3.0 . In contrast, in the arrangement of Figure 2 the ratio is 1.4.

The conclusion for this analysis is that poor instrument design leads to misleadingly high values of I_0 , artificially low detection limits for ΔOD and unnecessarily inhomogeneous transient concentration.

A simplistic analysis of the arguments above would lead to the conclusion that an extremely narrow monitoring beam (d approaching zero) would offer the best experimental solution. Not so. In principle, I_0 decreases with the square of the monitoring beam size “ d ”. The dependence is somewhat attenuated by the fact that large beams are more difficult to collect quantitatively. Further, very narrow monitoring beams force the near-focusing of the laser beam and as a result tend to promote transient-transient reactions and two-photon (or biphotonic) processes. In general, a monitoring beam diameter of 2-3 mm offers a good compromise.

Choosing a monitoring source: The monitoring source of choice is almost always a high-pressure xenon lamp. These lamps are used in vertical and horizontal arrangements, as shown in Figure 7.



The arrangement of Figure 7A is less efficient collecting light, largely because of difficulties covering a large solid angle with the mirror. Horizontal arrangements, either external (Figure 7B) or internal (Figure 7C) offer more effective light collection and can use either elliptical or parabolic mirrors. Elliptical mirrors yield focused beams and parabolic mirrors collimated beams. Horizontal lamps always produce a shadow from the front electrode at the center of

the beam. There are three solutions to this problem: (a) accept a beam with a central ‘black’ spot, which is unable to report on transients at the key spot at the center of the sample, (b) use an off-center alignment, greatly reducing the light throughput through the sample and (c) couple the beam with optical fibers, which effectively homogenize the beam and eliminate the electrode shadows. Luzchem uses Cermax ceramic lamps; these efficient HID Xenon lamps have very small electrodes and efficient internal mirrors, producing a remarkable 34 W radiant output with a 175 W lamp.

Delivering the monitoring beam: The analysis or monitoring beam needs to be coupled with the sample cuvette as shown in Figures 2 and 3. Conventionally, several lenses before and after the sample shape the beam through the sample compartment and deliver it to the monochromator slit.

Luzchem’s patented system uses optical fibers to deliver light to a collimator, which delivers the monitoring light to the sample cell and then to a pick-up fiber. A key characteristic of Luzchem’s system (Figure 8) is that no lenses are used between the sample and the pick-up fiber (region A in Figure 8). This is important because the polished fiber tip covers a remarkably small solid angle and therefore rejects well fluorescence, Raman signals or scattered light.

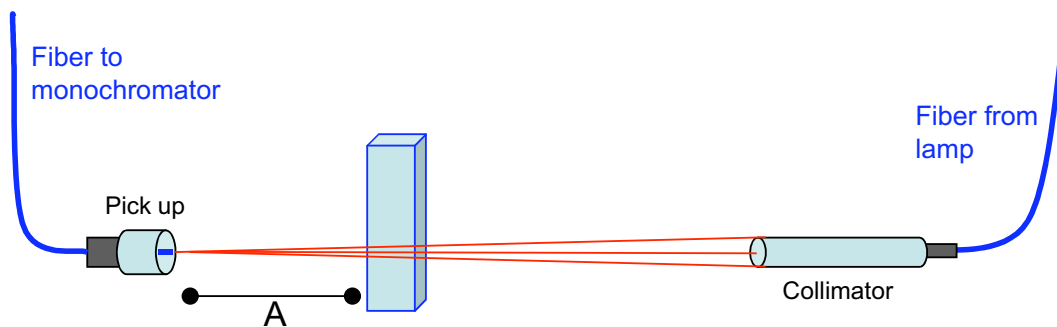


Figure 8: Luzchem’s patented beam arrangement at the sample compartment

Effective coupling in Luzchem’s system requires a judicious selection of lenses for the collimator, fiber numerical aperture and other optical design parameters. In conventional



systems, the lenses located after the sample contribute to collect fluorescence, Raman signals and scattered light, all of them causes of interference with short lived absorption signals.

Luzchem has designed a state-of-the-art nanosecond laser flash photolysis system, taking advantage of new technologies and its vast experience with the technique of nanosecond laser flash photolysis.

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