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SINGLE-PHOTON SYSTEMS APPLICATION NOTE

Singlet Oxygen Detection

August 2015

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Introduction

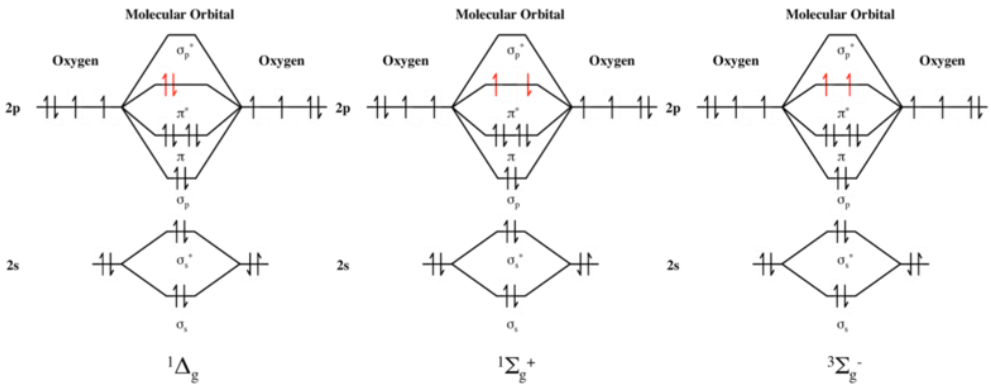
We describe how singlet oxygen fluorescence can be observed and quantified using an ID230 detector[1] together with an ID900 Time Controller.

The dosimetry of singlet-oxygen, through its luminescence at 1270nm, is a challenging task due to the low efficiency of the process and consequently extremely low light emission levels. Photomultipliers have traditionally been used for this purpose but these devices have low efficiencies, high noise and are sensitive to ambient light and are not fiber-coupled, precluding their use in some scenarios. More recently, super-conducting nanowire detectors have achieved sufficiently low noise to directly detect singlet-oxygen luminescence, but have the disadvantage of requiring advanced cryogenic cooling and having a small active area of approximately 100µm2 (single-mode fibre). On the other hand, the ID230 offers the same low noise, efficiencies of up to 30%, does not require cryogenic cooling and works with multimode fibers, resulting in a collection area of 10'000µm2, and therefore a 100x stronger observed signal.

Singlet Oxygen

Singlet oxygen is a highly reactive oxygen species, and plays an important role in several fields: physics, chemistry, biology, atmospheric science and medicine, and in particular in photo-dynamic therapy. Direct detection of singlet-oxygen is done through its phosphorescence, although this emission is extremely weak, it remains the preferred method of detection, as it provides artifact-free data and instant results.

Figure 1 : Molecular orbital scheme or the three electronic configurations of molecular oxygen, O2. Shown from left to right are: The singlet oxygen a^{1}Δg excited state, the singlet oxygen b^{1}Σg+ excited state, and the triplet ground state X^{3}Σg–. The 1s molecular orbital is omitted for simplicity. Note that the states only differ in the spin and the occupancy of oxygen's two degenerate antibonding πg-orbitals. Source: Wikipedia / Angelo Frei



[1] Customization available on request

The ID230 detector

Until recently, near infrared (NIR) single photon avalanche photodiodes have had noise levels of several thousand counts per second (cps) for single-mode (9µm) fiber detectors, and more for devices with large-core fibers. The ID230 is a breakthrough in detector technology, with <20 Hz cps noise in the ULN version, and fibers with a core diameter of up to 100µm. Fiber detectors are practical for several reasons: they allow to eliminate noise by having well-defined acceptance angles and positions and offer superior flexibility in the experimental layout, allowing the fiber to be moved freely for in-vivo experiments. An optical fiber can also collect light efficiently by being placed inside a sample.

Singlet-oxygen fluorescence is often detected after an excitation by a strong laser pulse, which can "blind" the detector for a few microseconds. To prevent the "blinding" from the excitation pulse, it is possible to modify the ID230 to accept a Gate signal, which ensures that the detector is off during the excitation pulse, and that it is turned on shortly (few hundred ns) after. This modification can be done on customer request.

The ID230 detector takes a single or multimode fiber as input, with an FC/PC connector. It outputs an electrical signal (LVTTL) over an SMA connector. An optional gate input may be added on special request, allowing the detector to be turned off during laser excitation.

ID220 and ID210 detectors

For experiments where the extreme low noise of the ID230 is not necessary, two other IDQ detectors are suitable: the ID220, which is similar to the ID230 but with noise levels of 1000 cps, is suitable for OEM applications, and the ID210 which also has higher noise levels , but can be gated very fast (<1ns gate rise-time). This gate can be used to turn off the detector during laser excitation and shortly after, to eliminate the initial "spike" in detected photons which can arise from fast-decaying fluorescence.

ID Quantique detectors vs Photomultipliers

Often, photomultipliers are used in Singlet-oxygen measurements. They have a large diameter active area and low quantum efficiency of order 2%, as well as a high noise (dark count) rate. ID Quantique detectors have 65µm fiber input, higher efficiency and much lower noise. The table below summarizes the differences between types of detectors.

	ID230	ID220	Photomultiplier
Coupling	Multimode fiber (NA=0.275)	Multimode fiber (NA=0.275)	Free-space
Detection efficiency	>25%	>20%	>1%
Dark count rate d)	<25 /s	<1000 /s	25000-250000 /s
Diameter of active area	65 µm (fiber)	65 µm (fiber)	18 mm
Maximum count rate	100'000 /s	100'000 /s	25'000'000 /s
Timing resolution	80 ps	200 ps	350 ps

Advantages of fiber-coupled detectors

Experimental noise is not solely determined by detector noise: to achieve high-sensitivity experiments, the detector must be isolated from environmental noise. Detectors with a large active area, such as photomultipliers, will be sensitive to ambient light, undesired fluorescence from optical elements and parts of the system which are not being investigated.

A fiber coupled-detector, on the other hand, has a small active area (fiber core), and a well determined numerical aperture. It is then possible to use a lens to image (focus) only the part of the system under investigation onto the fiber, rejecting a large part of ambient noise and spurious fluorescence. This, together with the extremely low dark count rates, and high detection efficiencies, enables experiments which are several orders of magnitude more sensitive than what could previously be achieved.

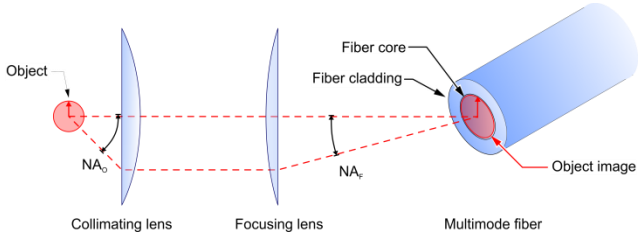
Coupling into multimode fiber

Coupling the Singlet Oxygen fluorescence light to fiber is done by imaging the "object", i.e. the volume illuminated by the excitation laser, onto the fiber core. This can be done with two lenses, as shown in Fig. 1. The first lens collimates the beam so that several optical elements, such as filters, can be placed along the beam path. The second lens focuses the beam onto the fiber core. If the object (illuminated volume) is smaller or larger than that of the fiber core (62.5 µm), it can be magnified or reduced by choosing collimating and focusing lenses of different focal lengths. For example, if the object has a diameter of 30µm, one would chose a collimating lens with a focal length of ½ that of the focusing lens, e.g. a f=40mm collimating lens and f=80mm focusing lens. The diameter of the lenses is chosen

to make use of the full NA of the fiber (NA_F=0.275). The lens radius R should be R>f x NA, which is R>80mm x 0.275 =22mm. Smaller lenses, with shorter focus distances, can be used if it is possible to place them closer to the object.

To align the experiment, a laser can be connected to the fiber instead of the detector, so that it can be back-propagated along the fiber, and focused onto the sample. This will guarantee good and easy alignment.

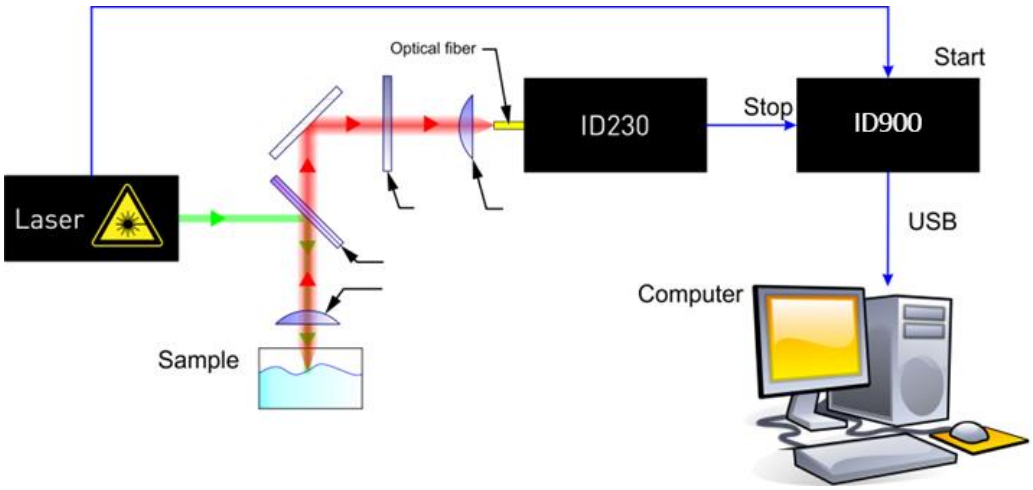
Figure 1: Imaging an object onto the fiber core. The collimating and focusing lenses can be chosen with different focal lengths, so that



Experiment

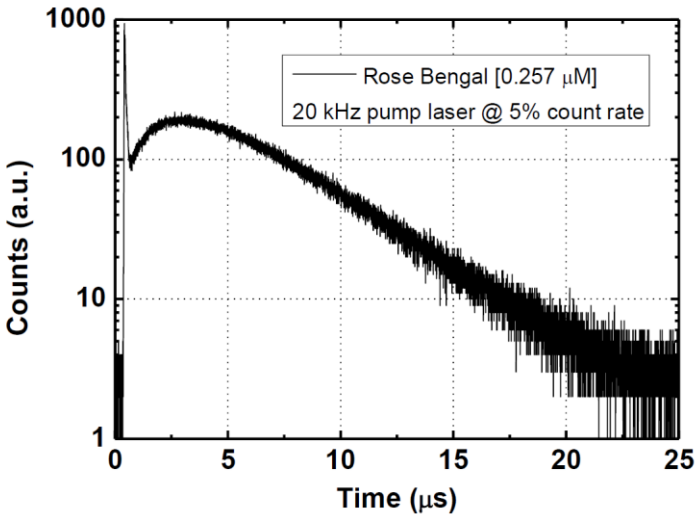
A typical experimental procedure (courtesy of Gianluca Boso , University of Geneva), is shown in Fig. 2. A pulsed green laser illuminates a sample, generating singlet oxygen. Fluorescence from this sample is collected via a dichroic mirror, and filtered as to reject unwanted light. Fluorescence photons are focused onto the fiber core and detected with an ID230 detector

Figure 2 : Typical experimental procedure. A pulsed excitation laser illuminates a sample. Fluorescence from this sample is collected through a dichroic mirror, and filtered as to reject undesired wavelengths. Light is then focused on a fibre and detected with an ID230 detector.



The delay between the laser pulse illumination and photon detection is measured with an ID900 Time Controller, and transferred to a computer to generate a histogram, plotted in Figure 3. The full details of this experiment can be found in (Boso, et al., 2015).

Figure 3 : Fluorescence rise and decay of singlet oxygen. The initial spike is due to fast-decaying el



References

Boso, G. et al., 2015. Low noise InGaAs/InP single-photon detector for singlet oxygen detection. *Quantum Sensing and Nanophotonic Devices XII,* Feb 2015.

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