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LUMINESCENCE FROM OPTICAL ELEMENTS COMMONLY USED IN NEAR-IR SPECTROSCOPIC STUDIES: THE PHOTOSENSITIZED FORMATION OF SINGLET MOLECULAR OXYGEN ($^1\Delta_g$) IN SOLUTION

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Summary

Upon excitation with visible light, optical elements made from silicon luminesce in the near-IR portion of the spectrum (1000 - 1300 nm). Excitation and emission spectra of optical grade silicon, recorded at 295 K, are presented in this report. The luminescence decay times depend both on the sample and on the experimental conditions. An emission spectrum of a Schott RG-850 filter is also reported. In most cases, interfering luminescence observed in time-resolved phosphorescence studies of singlet molecular oxygen ($O_2(^1\Delta_g)$), created by pulsed excitation of a sensitizer, can be attributed to the presence of optical elements which absorb visible radiation and subsequently emit in the near IR: either a silicon window, an interference filter containing a silicon blocking filter, or a standard colored glass filter.

1. Introduction

It has recently become feasible to detect the near-IR phosphorescence of singlet molecular oxygen ($O_2(^3\Sigma_g^-) \leftarrow O_2(^1\Delta_g)$) in a solution phase photosensitized reaction [1 - 10]. The $O_2(^1\Delta_g)$ emission spectrum is broad and structureless (full width at half-maximum (FWHM), about 30 nm) with $\lambda_{max} = 1270$ nm (7874 cm^{-1}, 0.98 eV) [1, 2, 8, 9]. This luminescence has been examined in various microsecond time-resolved studies in which the photosensitizer was excited by a pulsed laser [3 - 7]. The results obtained from these experiments have been used in studies of $O_2(^1\Delta_g)$ decay dynamics [8 - 10]. The intensity of the time-resolved $O_2(^1\Delta_g)$ phosphorescence signal has also been used to quantify the efficiency of $O_2(^1\Delta_g)$ formation in a photosensitized reaction [11 - 16]. In these photosensitized experiments, the desired 1270 nm $O_2(^1\Delta_g)$ signal must be isolated from both scattered laser light and sensitizer fluorescence. In many cases, the latter can be quite

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intense, particularly at the excitation laser powers routinely used (about 1 MW). Visible absorbing, IR transmitting cut-off filters have traditionally been employed to solve this problem. In particular, silicon does not transmit wavelengths shorter than about 1100 nm (*vide infra*) and, when supplemented with an antireflective coating for 1270 nm, it is seen to provide the perfect filter material. Nevertheless, despite the use of often sophisticated optical elements designed to eliminate interference at wavelengths other than 1270 nm, investigators in this field have been plagued by unwanted radiation which contributes to the observed near-IR signal. This background luminescence appears as a spike which is coincident with the laser pulse. For some common $O_2(^1\Delta_g)$ photosensitizers, the near-IR detection systems currently in use (response time constant, about 1 - 5 μs) are not fast enough to resolve a weak interfering signal from the $O_2(^1\Delta_g)$ luminescence. When certain porphyrins are used as photosensitizers, however, the background spike is often so intense that it can totally dominate the $O_2(^1\Delta_g)$ signal [7, 15, 17]. Nevertheless, since most of this work has addressed $O_2(^1\Delta_g)$ decay dynamics on a microsecond time scale [3 - 10], the existence of a nanosecond background spike has not been an issue.

We have recently completed the construction of a nanosecond, time-resolved near-IR spectrometer which is capable of monitoring the dynamics of $O_2(^1\Delta_g)$ formation in a photosensitized process [18, 19]. In order to comment correctly on processes which result in the formation of $O_2(^1\Delta_g)$, therefore, it has been necessary to characterize and subsequently eliminate the background signal which interferes with $O_2(^1\Delta_g)$ phosphorescence. In addressing this problem, we were quite surprised to discover that optical engineers were unable to provide us with information on the response of optical grade silicon to both UV and visible radiation. Since silicon blocking filters are an important part of our optical system, the study presented in this report was undertaken.

2. Experimental details

The nanosecond time-resolved near-IR detection system used in this work has been previously described [18, 19]. A Quanta–Ray PDL-2 dye laser–Quanta–Ray DCR-2 Nd:YAG laser system was used as a light source for all experiments. $O_2(^1\Delta_g)$ was created by the pulsed excitation of several sensitizers at either 355 nm or 532 nm (*vide infra*). The excitation spectra (Fig. 1) were recorded using the following laser dyes (Exciton) in the Quanta–Ray PDL-2: stilbene 420, coumarin 460, coumarin 480, rhodamine 590 chloride, and LDS 698. Both the second (532 nm) and third (355 nm) harmonics of the Nd:YAG laser were also used. The emission spectra (Fig. 2) were recorded using 700 nm (LDS 698) excitation. Although some amplified spontaneous emission is present in the dye laser output, we have insured that our excitation pulse is monochromatic by passing the laser beam through a dispersing prism followed by several slits. For the data in Figs. 1 and 2, the

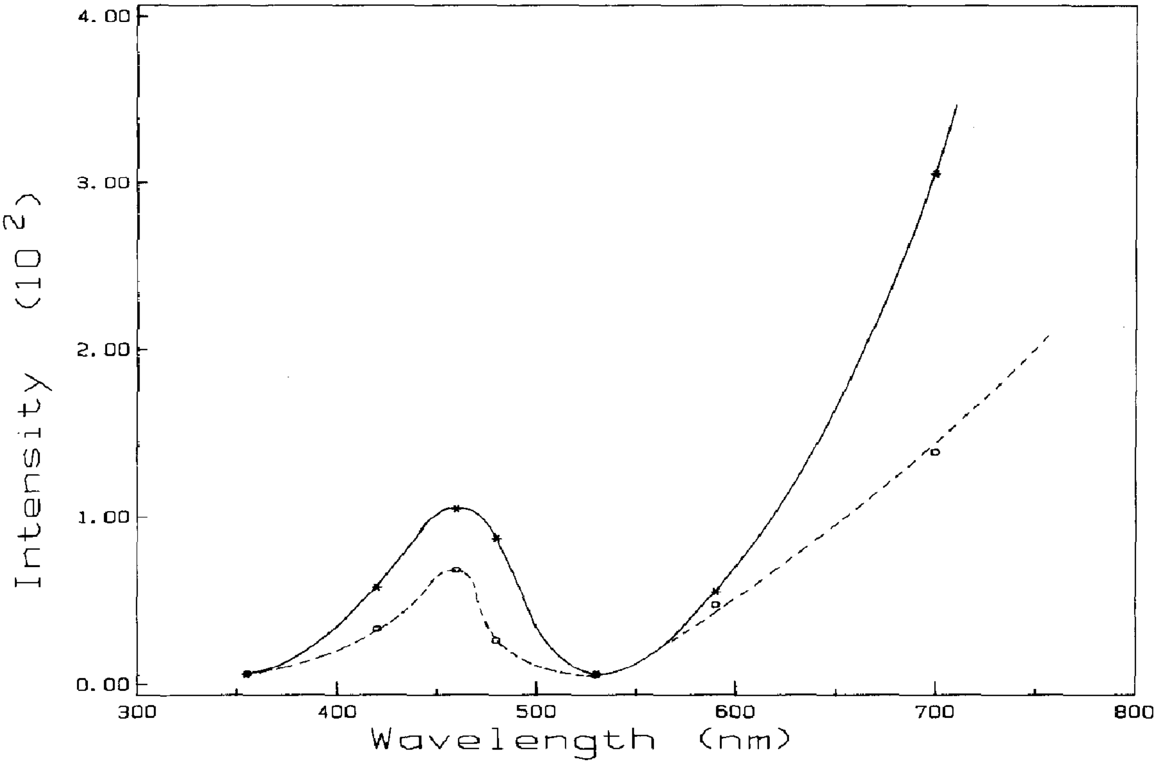

Fig. 1. Excitation spectra for the 3 mm thick, AR coated silicon window (— — —) and the 250 μm thick, uncoated silicon element (———). Luminescence was monitored at 1270 nm. At each wavelength, the laser energy incident on the silicon surface was 0.3 mJ pulse^{-1}.

laser output was attenuated with neutral density screens, sent through a limiting aperture and scattered off a partially reflective surface (about 10%) onto the optical element to be examined. At all wavelengths, the laser energy was 3 mJ pulse^{-1} at the 10% reflective surface. Therefore a pulse with an FWHM of about 5 ns at about 0.3 mJ pulse^{-1} was scattered onto a 0.5 cm × 0.5 cm area of the silicon windows and the colored glass filter. (Although it is difficult to quantify accurately the energy incident on the optical filters from sensitizer fluorescence, the laser energies used in this study are seen to represent adequately conditions in a photosensitized $O_2(^1\Delta_g)$ experiment.) The angle of incidence was 90°. A monochromator with a near-IR grating (Oriel models 7240 and 7272; blaze wavelength, 1000 nm; 600 lines mm^{-1}) provided spectral resolution. A silicon window was placed at the output slit of the monochromator to eliminate interference from visible light. Luminescence lifetimes were determined by deconvoluting [16, 19] the laser pulse profile from the observed signal. The two response components of our near-IR detection system [18, 19] are 25 ns and 860 ns. Laser energies were determined with a Scientec model 38-0101 volume absorbing disk calorimeter.

Two samples of silicon were studied: (1) an intrinsic (undoped) single-crystal element with an antireflective coating for 1270 nm (3 mm thick,

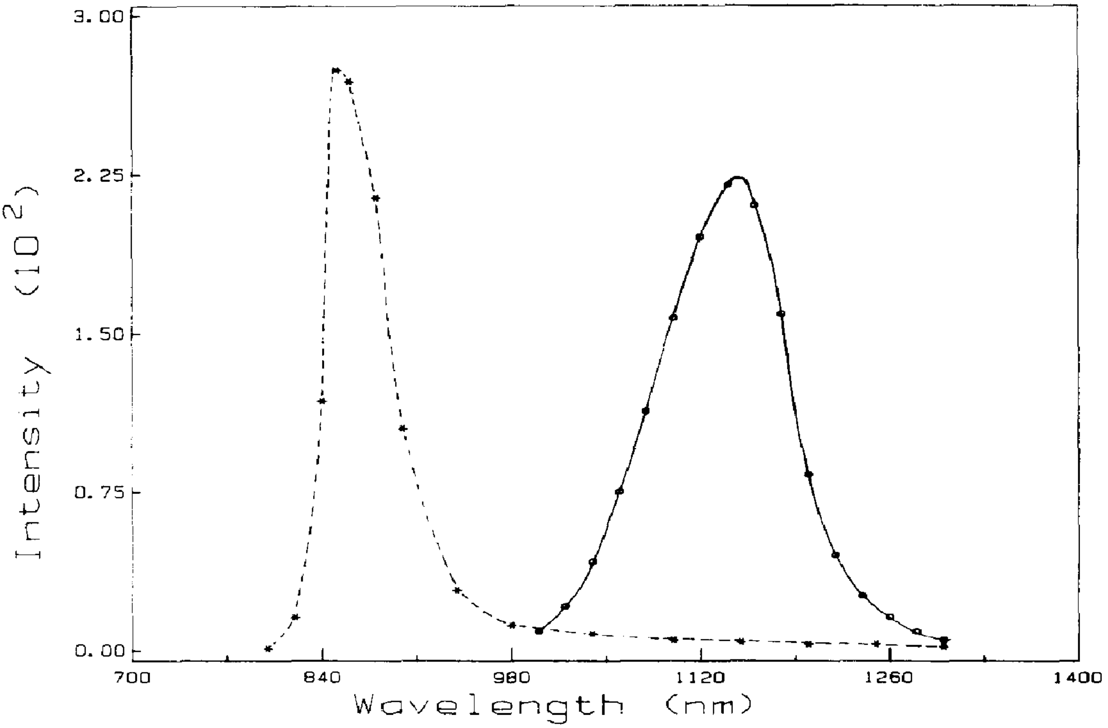

Fig. 2. Emission spectra observed from a sample of silicon 250 μm thick (———) and a Schott RG-850 colored glass filter (— — —) with excitation at 700 nm. The sample temperature was 295 K. At about 0.3 mJ pulse^{-1} excitation energy, the intensity of luminescence from the Schott filter was approximately three times larger than that observed from the 250 μm silicon element. Intensities have not been normalized to the detector spectral response function (germanium p–n junction detector) [18]. The spectra have been rescaled for comparison.

2.5 cm diameter, CVI Corporation) and (2) an n-type, phosphorus-doped uncoated single-crystal element (250 μm thick, 4 cm diameter). Other than routine washing with organic solvents, steps were not taken to clean the surface of the uncoated element. Consequently, it is likely that an oxide coating had developed in the course of normal exposure to the atmosphere. An interference filter centered at 1270 nm was used to isolate $O_2(^1\Delta_g)$ luminescence (Barr Associates; 70% transmittance; FWHM, 50 nm). Incorporated in this element is a silicon blocking filter. In addition, a 5 cm × 5 cm Schott RG-850 polished glass filter (3 mm thick) was examined. All experiments were performed at 295 K.

Acridine (Aldrich) was recrystallized three times from ethanol–water and sublimed under vacuum. 9,10-Dicyanoanthracene (DCA, Eastman Kodak) was recrystallized three times from ethanol–water. *meso*-Porphyrin IX dimethyl ester (MP9, Porphyrin Products) was used as received. Benzene (Fisher-Spectranalyzed$^{(R)}$) was refluxed over P_2O_5 and distilled prior to use.

3. Results and discussion

Three examples of the near-IR signal observed through our 1270 nm interference filter (with the silicon blocking element) subsequent to pulsed laser excitation of a sensitizer are shown in Fig. 3. Both acridine ($\phi_{\text{fluores}} = 5 \times 10^{-4}$ [20], λ_{max}(fluores) $\approx$ 420 nm [21]) and DCA ($\phi_{\text{fluores}} \approx 0.9$ [11, 22], λ_{max}(fluores) $\approx$ 440 nm, 470 nm [23]) were irradiated at 355 nm (16 mJ pulse^{-1}). MP9 ($\phi_{\text{fluores}} = 0.08$ [24], λ_{max}(fluores) $\approx$ 620 nm, 690 nm [24, 25]) was irradiated at 532 nm (30 mJ pulse^{-1}). In each case, a background spike is clearly visible and obscures a portion of the $O_2(^1\Delta_g)$ signal. The spike is not due to r.f. noise from the laser. In all cases, the intensity of the spike is correlated to both the intensity and the wavelength of sensitizer fluorescence incident on the optical filter. For example, with DCA and MP9, both of which have singlet states that can be quenched by oxygen [11, 16, 19], the intensity of the background spike decreases as the oxygen concentration is increased. For sensitizers that have a red fluorescence (*e.g.* porphyrins), a solvent-induced red shift in the emission spectrum results in a corresponding increase in the intensity of the background spike. Transmission of the visible dye fluorescence through the filter element is not responsible for the interfering signal. In fact, the absorption coefficient for silicon at 300 K is quite large at wavelengths less than about 1000 nm [26 - 28]. (The absorption spectra for silicon and germanium in ref. 27 are incorrectly labelled. See ref. 26. The spectra reported are for single-crystal silicon.)

Since many colored glass filters are known to luminesce upon UV and visible irradiation, we suspected that the same might be true of the silicon in our filter elements. Indeed, upon excitation at 700 nm we were able to record identical emission spectra (λ_{max} = 1150 nm; FWHM, 110 nm) from both silicon samples (Fig. 2). The intensity of luminescence from the element 250 μm thick, however, was approximately two times larger than that from the 3 mm element. Our results compare favorably with published data on both intrinsic and extrinsic single-crystal silicon radiative recombination [29 - 34]. (Most of the single-crystal spectra were recorded at low temperatures (below 100 K). At these temperatures, discrete bands are observed. However, the broad structureless spectrum for silicon reported in Fig. 2 compares quite well with the thermally broadened single-crystal spectrum reported by Haynes *et al.* [29] at 215 K.) The emission spectrum obtained when a Schott RG-850 filter was irradiated at 700 nm is also presented in Fig. 2 for comparison (λ_{max} = 850 nm). In both cases, the luminescence intensity at 1270 nm is significant.

The decay of silicon luminescence depends both on the sample examined and on the experimental conditions. For example, under the conditions in which the data in Figs. 1 and 2 were recorded (*vide supra*), the decay of luminescence was biexponential for both the 3 mm and the 250 μm samples. In each case, the fast component of decay was found through our deconvolution routine to be less than our near-IR detector response function of 25 ns

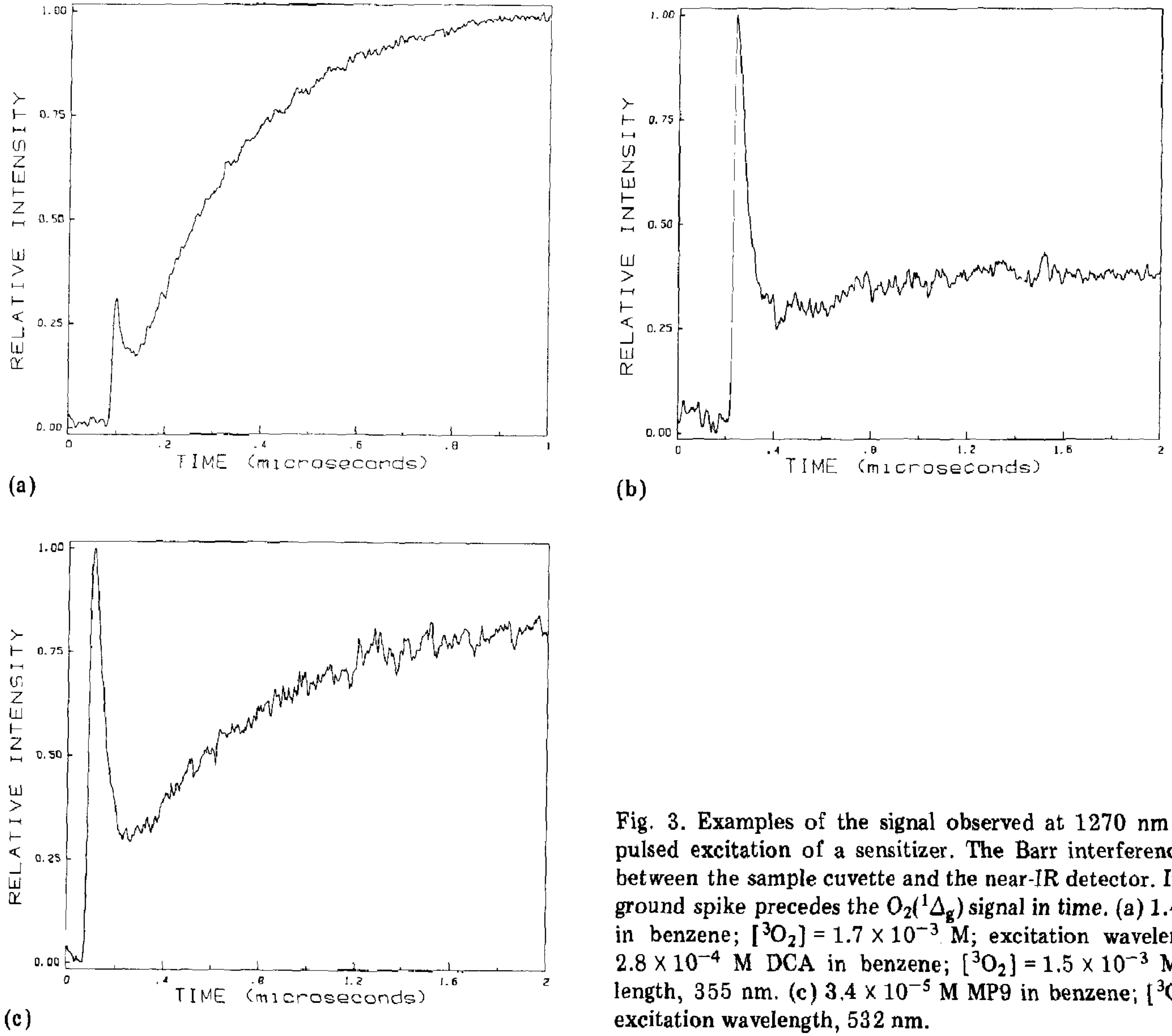

Fig. 3. Examples of the signal observed at 1270 nm subsequent to the pulsed excitation of a sensitizer. The Barr interference filter was placed between the sample cuvette and the near-IR detector. In each case, a background spike precedes the $O_2(^1\Delta_g)$ signal in time. (a) 1.4×10^{-4} *M* acridine in benzene; $[^3O_2] = 1.7 \times 10^{-3}$ M; excitation wavelength, 355 nm. (b) 2.8×10^{-4} M DCA in benzene; $[^3O_2] = 1.5 \times 10^{-3}$ M; excitation wavelength, 355 nm. (c) 3.4×10^{-5} M MP9 in benzene; $[^3O_2] = 1.7 \times 10^{-3}$ M; excitation wavelength, 532 nm.

[18, 19] ($\tau \approx 10$ ns; excitation wavelength, 700 nm; monitored at 1150 nm). The slow component lifetimes differed slightly (about 115 ns for the 3 mm element and about 220 ns for the 250 μm element). In both cases, however, the extent to which the slow component contributes to the overall decay function is substantially less than the contribution from the fast component (the ratio of pre-exponential factors, slow to fast, is 8×10^{-2}). As the intensity of excitation light incident on the silicon was increased, the lifetimes for both the fast and the slow components of decay decreased (*i.e.* the rate of luminescence decay increased). The extent to which the slow component contributed to the overall decay function remained unchanged. The decay of silicon luminescence was also found to depend on the wavelength at which emission was monitored. In particular, at 1230 nm the lifetime of the slow component in both samples was slightly less than that determined at 1150 nm. More importantly, however, the slow component was found to contribute less to the overall decay function (ratio of pre-exponential factors, slow to fast, is 3×10^{-2}). In other words, the luminescence decay is beginning to approach a single exponential function. Observed lifetimes do not change substantially with a change in excitation wavelength. Under conditions in which the $O_2(^1\Delta_g)$ signal is monitored, sensitizer fluorescence from a nitrogen-purged sample incident on the Barr interference filter (1270 nm) results in a silicon decay function which is single exponential. If the sensitizer fluorescence lifetime is approximately 15 ns, or less (*e.g.* acridine in benzene [19] or DCA [16]), the observed decay time is simply the response function of our near-IR detector (25 ns). In general, the silicon luminescence lifetimes observed are comparable with values published by Cuthbert (single-crystal intrinsic silicon at 1.8 K) [33, 34]. Using a silicon photodiode as an optical detector (response time, about 5 ns), the Schott RG-850 luminescence (measured at 850 nm) did not broaden our laser pulse (FWHM, about 5 ns). Therefore, we suggest that the RG-850 luminescence lifetime is of the order of one nanosecond or less.

With the silicon luminescence monitored at 1270 nm (interference filter), excitation spectra were recorded for both silicon windows (Fig. 1). The data show a broad absorption at the blue end of the spectrum ($\lambda_{max} \approx$ 460 nm) and a sharp rise in absorption at longer wavelengths. The blue–UV absorption was not expected simply on the basis of published transmission spectra [26 - 28]. This band may be due to either a slight change in silicon reflectance as a function of wavelength or to an oxide and/or impurity coating on the surface. Nevertheless, it is now quite evident why both the blue fluorescing $O_2(^1\Delta_g)$ sensitizers (*e.g.* DCA) and the red fluorescing $O_2(^1\Delta_g)$ sensitizers (*e.g.* MP9) give rise to an intense near-IR background spike (Fig. 3).

4. Conclusions

Time-resolved, near-IR spectroscopic studies of $O_2(^1\Delta_g)$ in solution are often perturbed by an intense background luminescence. On the nanosecond time scale, this interfering signal can, in many cases, preclude an accurate analysis of $O_2(^1\Delta_g)$ formation dynamics in an energy transfer process from a photosensitizer. This background signal can be attributed, in most cases, to the luminescence of silicon, commonly used as a blocking filter in front of the near-IR detection system. We suggest that visible sensitizer luminescence is absorbed by the silicon filter which in turn luminesces in the near IR. We have reported emission and excitation spectra which support our hypothesis. The solution to this problem is seen to involve the use of highly reflective cold mirrors whose coatings do not luminesce in the near IR.

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