

THE CHARACTERIZATION OF GERMANIUM p-n JUNCTION DETECTORS FOR USE IN NANOSECOND TIME-RESOLVED NEAR-IR SPECTROSCOPIC STUDIES: THE PHOTOSENSITIZED FORMATION OF SINGLET MOLECULAR OXYGEN ($^1\Delta_g$) IN SOLUTION

KAI-KONG IU, RODGER D. SCURLOCK and PETER R. OGILBY†

Department of Chemistry, University of New Mexico, Albuquerque, NM 87131 (U.S.A.)

(Received May 3, 1986; in revised form July 8, 1986)

Summary

A nanosecond time-resolved near-IR spectrometer has been constructed for the purpose of resolving events that result in the solution-phase, photosensitized formation of singlet molecular oxygen ($O_2(^1\Delta_g)$). A germanium p-n junction detector is used to monitor the 1270 nm phosphorescence of $O_2(^1\Delta_g)$. The response of several commercially available germanium detectors to pulsed radiation has been studied. The time dependence of the observed photocurrent is discussed in terms of semiconductor charge carrier dynamics. The detector response is represented in a general functional form which can subsequently be used in a deconvolution routine to extract information on the rate of $O_2(^1\Delta_g)$ formation.

1. Introduction

The photochemistry and photophysics of singlet molecular oxygen ($O_2(^1\Delta_g)$) has been studied for many years [1, 2]. It has recently become feasible to detect the near-IR phosphorescence of $O_2(^1\Delta_g)$ ($O_2(^3\Sigma_g^-) \leftarrow O_2(^1\Delta_g)$; 1270 nm) in a solution-phase time-resolved experiment [3 - 7]. This technique has subsequently become indispensable in studies of $O_2(^1\Delta_g)$ decay dynamics [8 - 10]. The success of these experiments was due, in a large part, to the use of germanium junction detectors whose responsivity at 1270 nm is appreciable (about 0.5 A W^{-1}) [11]. Unfortunately, however, the response time of the detection systems in the studies cited above was limited to approximately 1 μs . This was due, primarily, to RC restrictions (*vide infra*) and preamplifier bandwidths. Consequently, a direct study of the dynamics of $O_2(^1\Delta_g)$ formation in a photosensitized process was precluded. The deactivation of excited state organic and biological molecules by molecular oxygen has long been the subject of scientific study [12 - 16].

† Author to whom correspondence should be addressed.

The mechanism, rate and efficiency of $O_2(^1\Delta_g)$ formation in this quenching reaction is of particular concern. Consequently, a probe capable of directly resolving events that result in the formation of $O_2(^1\Delta_g)$ is seen to be an extremely important tool.

Using an InGaAs detector [17], Parker and Stanbro have recently been able to resolve submicrosecond events in the porphyrin-sensitized production of $O_2(^1\Delta_g)$ [18]. Using commercially available, low cost germanium p-n junction detectors similar to those used in earlier studies [3-10], we have also completed the construction of a time-resolved, near-IR spectrometer capable of monitoring the dynamics of $O_2(^1\Delta_g)$ formation. We discovered, however, that our data contained detector-related artifacts which interfered with the $O_2(^1\Delta_g)$ signal. Consequently, we have been particularly concerned with characterizing the performance of these germanium detectors under conditions which approximate an $O_2(^1\Delta_g)$ phosphorescence experiment. We have discovered that tests typically used by photochemists to characterize semiconductor junction devices may not accurately represent the often complicated response of these elements to pulsed radiation. In this report, we discuss the general response characteristics of these germanium p-n junction detectors and present a method by which this response may be considered in studies of $O_2(^1\Delta_g)$ formation.

2. Experimental details

Four different germanium p-n junction detectors were examined in this study; a 2 mm² element (Judson Infrared, Inc., J16-5sp), two 1 mm² elements (Judson Infrared, Inc., J16-18 and Opto-Electronics, Inc., GD8) and a 0.25 mm² element (Opto-Electronics, Inc., GD10). The elements were reverse biased (2 mm² \equiv 3 V, 1 mm² \equiv 9 V, 0.25 mm² \equiv 9 V) and placed in series with a load resistor (180 Ω). A 100 MHz unity gain buffer amplifier (LH0033) was used to drive a 50 Ω coaxial cable. All components were mounted on a printed circuit board. In order to facilitate detector interconversion, small plug-in sockets were used as an alternative to directly soldering the detector leads into the circuit. Within the time resolution of our study, this did not seem to influence adversely the stray capacitance of our system. Signals were amplified by a Comlinear CLC100 component (20 dB gain) and digitized for subsequent analysis (Tektronix 7912 AD interfaced to an IBM personal computer).

Two different light sources were used to create excess charge carriers in the detectors. An AlGaAs diode laser (820 nm), driven by a Hewlett-Packard model 214A pulse generator, was used to create a highly reproducible step function of variable width. A fiber optic was mounted at the laser in order to facilitate delivery of the optical pulse to the detector under study. The rise time of the electrical driving pulse (10% - 90%), averaged over 16 shots in order to accommodate any jitter broadening that would appear under experimental conditions, was 15 ns. The fall was slightly

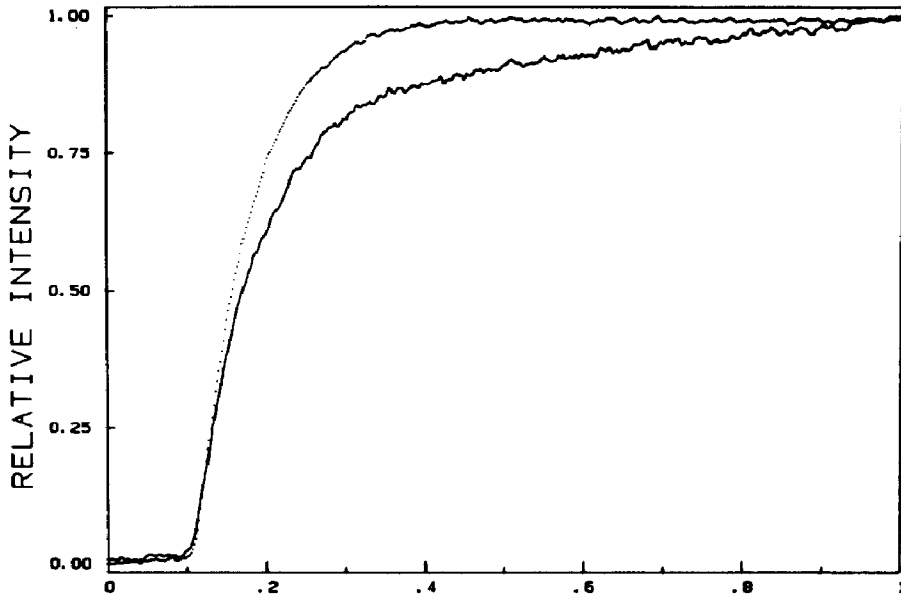
slower (about 20 ns). Using a reverse-biased silicon detector (50 Ω load) as a monitoring device, the optical pulse of the diode laser was seen to reproduce the electrical driving pulse quite well. Detector response was quantified at various AlGaAs laser diode pulse widths (*vide infra*). The limit of the smallest pulse width available in our laboratories is the fundamental output of a Quanta Ray DCR-2 Nd:YAG laser (full width at half-maximum (FWHM), about 8 ns at 1060 nm). The beam was sufficiently attenuated by multiple scattering off of optical surfaces and by the use of neutral density filters.

For the work reported in this paper, $O_2(^1\Delta_g)$ was created by the pulsed excitation (355 nm, third harmonic of Nd:YAG) of acridine (1×10^{-4} M) in an oxygenated benzene solution. The 1270 nm $O_2(^1\Delta_g)$ phosphorescence, monitored at 90° to the excitation pulse, was isolated by a silicon window AR coated for 1270 nm (CVI Corporation) and an interference filter centered at 1270 nm (Barr Associates; 70% transmittance; FWHM, 20 nm).

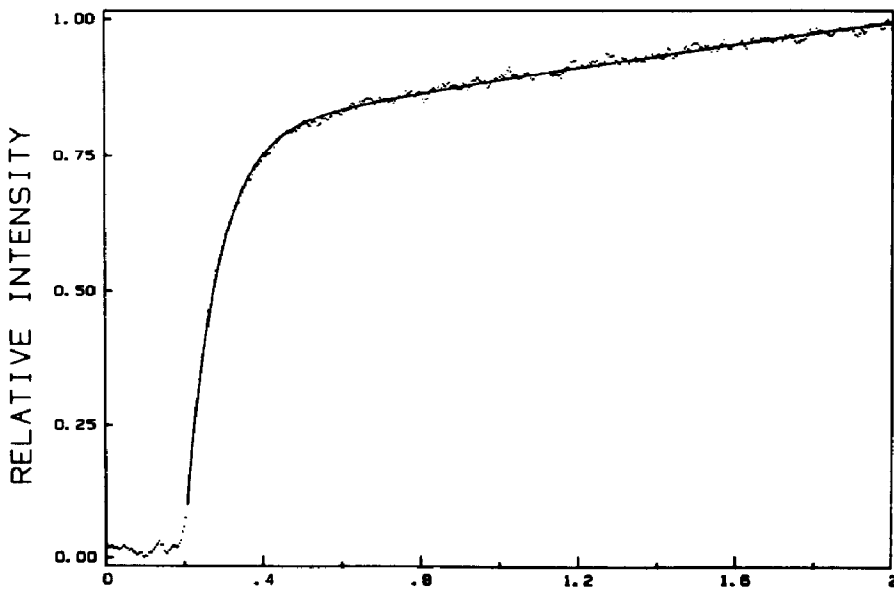
3. Results and discussion

3.1. Judson elements

Upon photoexcitation with the AlGaAs laser diode, the observed detector response depended significantly on the position of the fiber optic terminus relative to the germanium element. When the terminus was up close and centered on the active (biased) region of the element, the observed signal was a step function whose rise and fall were dampened only by an apparent RC effect. For the 2 mm² element, a single-exponential fit to the data yielded $\tau = 80$ ns. However, if the fiber optic terminus was pulled back slightly or translated to one side such that portions of the non-active (no or low bias) region of the detector were irradiated, a much slower second component ($\tau = 1.8 \mu\text{s}$ for 2 mm² element) appeared on both the rise and the fall (Fig. 1). The extent to which this slower component contributed to the overall response was directly related to the amount of light incident on the non-active detector region. Despite a much smaller junction capacitance which would give rise to a faster high frequency 3 dB limit (*vide infra*), the observed detector response for the 1 mm² element was actually worse than that for the larger 2 mm² element. Although visual inspection of the elements indicates that the ratio of the non-active area to the active area for the 1 mm² element is approximately the same as the corresponding ratio for the 2 mm² element, it is quite reasonable to assume that the ratio of the *illuminated* non-active area to the *illuminated* active area in the 1 mm² element is substantially larger than that in the 2 mm² element. Consequently, the total rise of the 1 mm² element is influenced more by the slow component. Although not as pronounced, this same phenomenon was also observed with the Opto-Electronics elements (Section 3.2). For wide excitation pulses (about 1 - 30 μs), the detector response was approximately symmetrical (*i.e.* the biexponential rise was mirrored by the biexponential



(a) TIME (microseconds)



(b) TIME (microseconds)

Fig. 1. (a) Response of a germanium detector (Judson 2 mm²) to an optical step function. When light is incident on the detector active area only (dots), the rise is RC limited with $\tau = 80$ ns. When a portion of the incident light falls on the non-active area (full line), a slower second component appears. The intensity of the latter trace has been rescaled to facilitate comparison on this time scale. Also see Fig. 6. (b) Double-exponential fit to the signal observed when a portion of the non-active area of the element is irradiated ($\tau_1 = 80$ ns and $\tau_2 = 1.8 \mu\text{s}$).

fall). As the pulse width was reduced to the extent that its magnitude was substantially less than the lifetime of the slow component on the rise, the response of both detectors showed the expected asymmetry; there was an apparent fast rise with a much slower biexponential decay. At the limit of an 8 ns FWHM pulse (Nd:YAG laser), the rate of detector relaxation showed an intensity dependence. At extremely low incident light intensities, a single exponential function ($\tau = 80$ ns for 2 mm² element, RC limit) was sufficient to characterize the decay. As the intensity was increased, however, the second slower exponential component ($\tau = 1.8$ μ s for 2 mm² element) seen at larger pulse widths began to contribute to the photocurrent (Fig. 2). As expected, if the system RC limit begins to approach the lifetime of the slow detector decay component, it is often difficult to see the latter, thereby giving the impression that one has a simple single-exponential decay function.

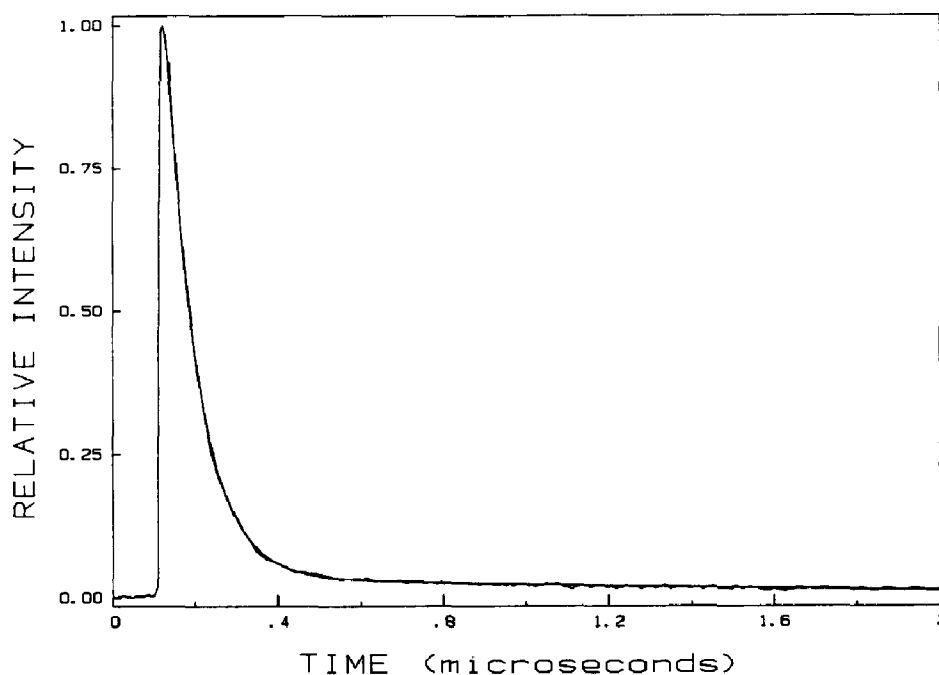


Fig. 2. Response of the Judson 2 mm² detector to a 1060 nm 8 ns FWHM pulse (Nd:YAG laser). Note that the slow component of decay is clearly visible ($\tau_1 = 80$ ns and $\tau_2 = 1.8$ μ s).

An adequate explanation for these results necessarily involves a discussion of the dynamics of semiconductor charge carriers. This can be a non-trivial exercise, particularly if the presentation is to be quantitative. In a simple, uniform, biased semiconductor, carrier densities will depend on several factors [19 - 26]: generation rate of the charge carriers, recombination (deactivation) of the charge carriers, electric field gradient in the element, diffusion of the charge carriers (electric-field independent) and drift

of the charge carriers (electric-field dependent). These terms are conveniently expressed in the continuity equations for both holes and electrons [19 - 21]. Under realistic non-ideal conditions, an observed detector response will be the convolution of many independent processes that vary from one germanium element to the next. For instance, recombination of holes and electrons in germanium is an indirect process [19, 20] involving trapping or recombination centers within the band-gap. Since any impurity or lattice defect in the material can serve as a trapping center, it is expected that recombination rates will be element dependent. This can also result in fall times that may be different from rise times [25]. In the work reported here, the most important complicating factor that influences the observed photocurrent is due to irradiation of both active (biased) and non-active (unbiased) areas of the detector. In the former case, the photocurrent will be determined primarily by mobility of carriers in the electric field (drift). This process is seen to be fast and will coincide with our RC limit. However, charge carriers generated in the non-active region will contribute to the photocurrent at a rate which is determined by diffusional processes. Consequently, the photocurrent induced by an optical step function may have a component which is much slower than the system RC limit, particularly if the charge carriers must diffuse over a long path length (Figs. 1 and 2). Our observation that the slow component of the detector response became more dominant as the amount of light incident on the non-active area was increased seems quite reasonable within the framework of this explanation. At the limit of a short, low intensity excitation pulse, it is not unreasonable to expect that the slow component of detector decay will be difficult to observe. In this case, charge carriers in the non-active region may recombine at trapping centers before they contribute to the observed photocurrent. As the light intensity is increased at this short-pulse-width limit, however, the concentration of charge carriers will likewise increase. As a result, the number of carriers that escape trapping and contribute to the photocurrent goes up. The observed signal, therefore, will begin to show, once again, a slower second exponential component (Fig. 2).

Although p-n junction detectors similar to those examined in this study have routinely been used with success in studies of $O_2(^1\Delta_g)$ decay dynamics [3 - 10], the lifetimes involved are usually long enough to preclude interfering artifacts from the slow component of detector relaxation. For submicrosecond studies, however, the problems presented above must be addressed. In order to resolve events that result in the formation of $O_2(^1\Delta_g)$, it is necessary to have a high frequency RC limit less than about 100 ns [27]. This RC limit is primarily determined by two factors: detector junction capacitance and the load resistor. Although junction capacitance is substantially reduced by a reverse bias on the element, capacitance is most effectively reduced by using smaller elements (less than 2 mm²). Similarly, although signal levels will suffer substantially, loads of low resistance must be used (200 Ω or less). In a photosensitized reaction, $O_2(^1\Delta_g)$ is typically generated in a 1 cm³ volume of solution [3 - 10]. It is difficult to trap

efficiently a substantial number of the near-IR photons radiating into a sphere from this volume and successfully focus them onto the small active area (less than 1 mm^2) of a germanium element. Nevertheless, it is still possible to mask the non-active area of an element or to couple the optical signal onto the active area of the element with a fiber and still have an appreciable signal-to-noise level. In both cases, complications from the slow detector component are minimized. Another alternative is to quantify the detector response in a control experiment such as those mentioned above, and to deconvolute this response from the observed $\text{O}_2(^1\Delta_g)$ signal [27]. Several points must be kept in mind if this approach is to be used. The response time of semiconductor elements can depend significantly on the wavelength of incident light. Because of changes in the semiconductor absorption cross-section, incident photons will have penetration depths which depend on their wavelength. Electrons and holes generated at different positions in the semiconductor will consequently have different travel times before contributing to the observed photocurrent. For germanium, whose absorption cross-section is larger at the blue end of the spectrum [21], it might therefore be expected that charge carriers generated by an AlGaAs diode laser (820 nm) would be closer to the surface of the element and would have farther to travel than carriers generated by an Nd:YAG laser (1060 nm) or $\text{O}_2(^1\Delta_g)$ (1270 nm). These differences in travel time could then be manifested in the experimentally observed rise time. For the range of wavelengths used in this work (820 - 1270 nm), however, there is evidence that rise times in germanium are fairly independent of wavelength [21]. Our experimental results support this conclusion. Response times determined in the laser diode (820 nm) control experiment are identical with those observed when the Nd:YAG laser (1060 nm) was used as the excitation source (Fig. 2). Results from some $\text{O}_2(^1\Delta_g)$ experiments presented below lead us to conclude that this wavelength independence extends out to 1270 nm. A second problem which must be addressed if the detector response is to be deconvoluted is the accuracy, in a control experiment, with which one can reproduce the extent to which $\text{O}_2(^1\Delta_g)$ luminescence falls on the non-active area. Although this problem is seemingly intractable, we have combined model calculations with some of our experimental results to show that it is easily solved within the framework of our deconvolution routine. The detector response is adequately expressed in the following functional form (Fig. 1(b)):

$$\text{detector response} = \exp(-k_{\text{fast}}t) + A \exp(-k_{\text{slow}}t) \quad (1)$$

The convolution [28 - 30] of eqn. (1) with a step function adequately models the experimentally observed detector response (Fig. 3). Conversely, a step function (Hewlett-Packard electronic driving pulse) may be deconvoluted from the observed detector response to yield values for the variables in eqn. (1). This process can be repeated for experimental response functions that arise from tests in which the ratio of the illuminated active area to the illuminated non-active area changes. For a specific element under these conditions, the only parameter in eqn. (1) which changes is the pre-exponen-

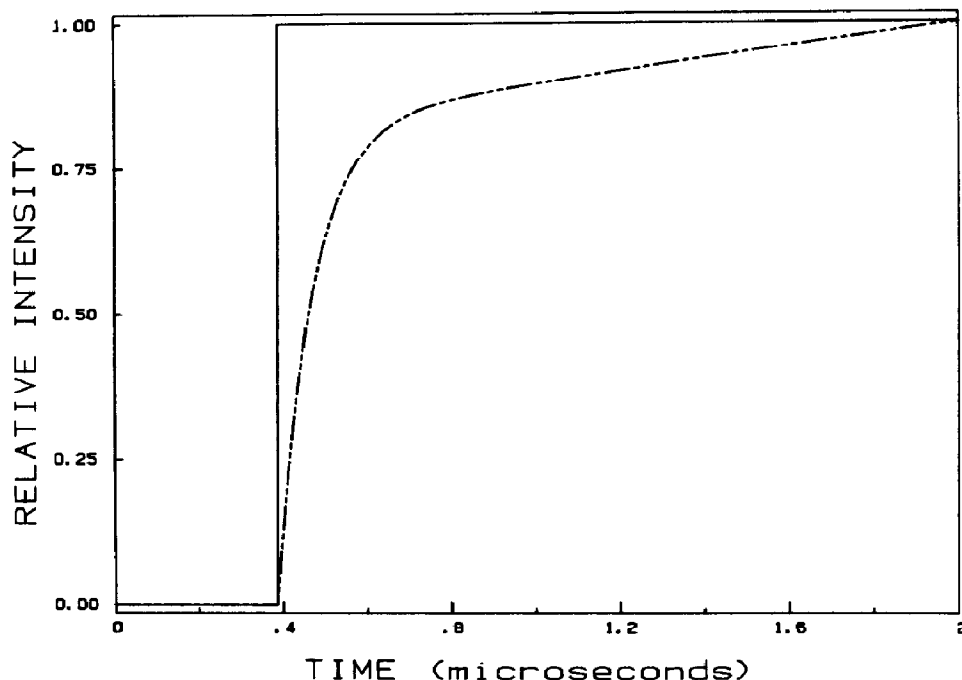


Fig. 3. The convolution of eqn. (1) ($\tau_1 = 80$ ns, $\tau_2 = 1.8$ μ s, $A = 0.01$) with a step function (full line). The latter trace has been rescaled to facilitate comparison on this time scale. The calculation adequately models the observed detector response.

tial factor A . This seems quite reasonable in the context of our earlier discussion where k_{fast} is determined by RC effects and k_{slow} by diffusion and recombination in the non-active area. It is possible, therefore, to quantify accurately a germanium p-n junction detector response under conditions where radiation is incident on both active and non-active areas of the element.

The concentration of $O_2(^1\Delta_g)$ as a function of time may be approximated, to a first order [18, 27], as a difference of two exponentials:

$$[^1O_2] = K\{\exp(-k_d t) - \exp(-k_r t)\} \quad (2)$$

The rate constant k_d for $O_2(^1\Delta_g)$ decay in solution, determined in independent experiments [3 - 10], is a known quantity. The rate constant k_r which expresses the rise of $O_2(^1\Delta_g)$ is the unknown parameter to be obtained. Consequently, the observed 1270 nm $O_2(^1\Delta_g)$ signal S_{obs} will be a convolution of the function that characterizes the detector response (eqn. (1)) with eqn. (2).

$$S_{obs} = K \int_0^t \{\exp(-k_d x) - \exp(-k_r x)\} [\exp\{-k_{fast}(t-x)\} + A \exp\{-k_{slow}(t-x)\}] dx \quad (3)$$

Using an iterative, non-linear least-squares deconvolution routine [27 - 31], the detector response function has been deconvoluted from an observed $O_2(^1\Delta_g)$ signal (Fig. 4). The calculation yields a value for k_r which can be used in a study of the dynamics of $O_2(^1\Delta_g)$ formation [27]. In the experiment cited in Fig. 4, at the limit of high oxygen concentration, the rate of $O_2(^1\Delta_g)$ formation begins to approach our RC limit of 80 ns (2 mm^2 element) [27]. Since the lifetime of $O_2(^1\Delta_g)$ in benzene is approximately $30 \mu\text{s}$ [8 - 10], our $O_2(^1\Delta_g)$ signal begins to approximate a step function. Under these conditions, the detector response is almost identical with the response when the 820 nm laser diode was used as the excitation source. We can therefore conclude that the time constant for the slow detector response component is independent of wavelength at the values of interest: 820 nm (control excitation) and 1270 nm ($O_2(^1\Delta_g)$ phosphorescence).

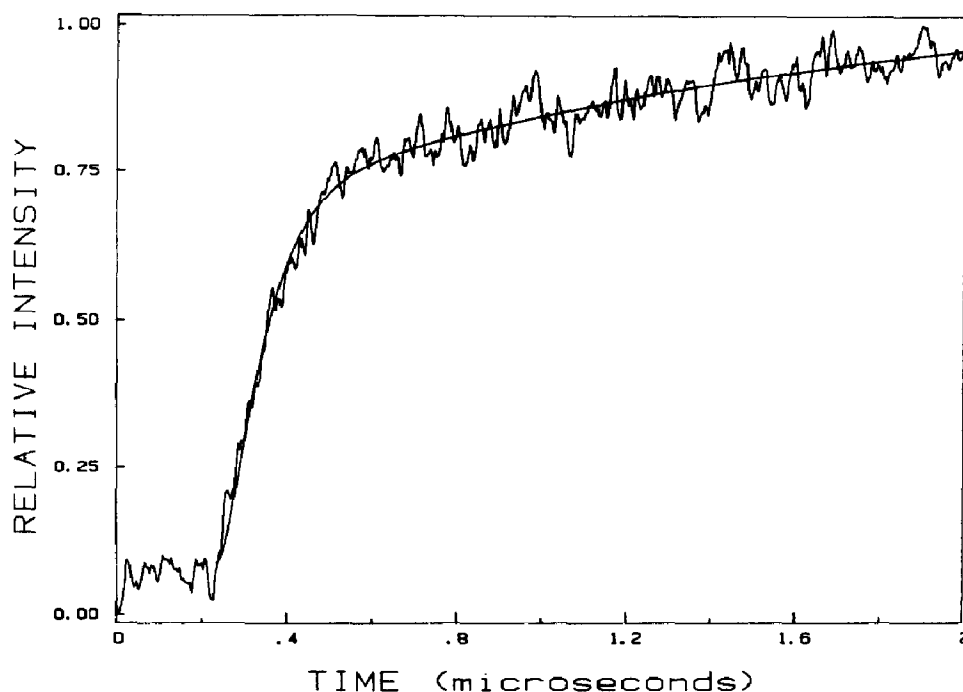


Fig. 4. Signal observed at 1270 nm ($O_2(^1\Delta_g)$) subsequent to the pulsed excitation (355 nm) of acridine in an oxygenated ($8 \times 10^{-3} \text{ M}$) benzene solution. The full line was calculated using the function in eqn. (3). The slow component of the detector response (Judson 2 mm^2 element) is clearly visible.

3.2. Opto-Electronics Elements

Most of our efforts have been directed towards characterizing detectors manufactured by Judson Infrared, Inc. This process has involved the inevitable comparison with elements manufactured by other companies. For the work reported here, a Judson 1 mm^2 element and an Opto-Electronics 1 mm^2 element were studied. In addition, a smaller (0.25 mm^2) Opto-Electronics element was examined. Identical conditions were preserved as

the elements were interchanged. Although not as pronounced as in the case of the Judson detectors, the observed response of the smaller Opto-Electronics device to an optical step function was not as good as the response observed from the corresponding larger element. Once again, we suggest that this is due to a much larger ratio of illuminated non-active area to illuminated active area in the smaller device. Consequently, any gains due to a lower junction capacitance are offset by a larger contribution from the slow diffusion related detector response. The 1 mm^2 Opto-Electronics element also showed a detector response that was related to the position of the terminus of the optical fiber carrying the excitation signal. When the fiber was up close and centered on the active area, an excellent representation of the electrical driving pulse was obtained. As the fiber was pulled away slightly, the expected second component appeared (Fig. 5). As mentioned earlier, it is important that the elements be examined under conditions that best approximate those in which $\text{O}_2(^1\Delta_g)$ is the source of incident radiation. Consequently, for the studies in which the Judson element was compared with the Opto-Electronics element, the terminus of the fiber optic carrying the excitation signal was positioned such that the entire element (both active and non-active areas) was irradiated. The data for a $1 \mu\text{s}$ excitation pulse is shown in Fig. 6.

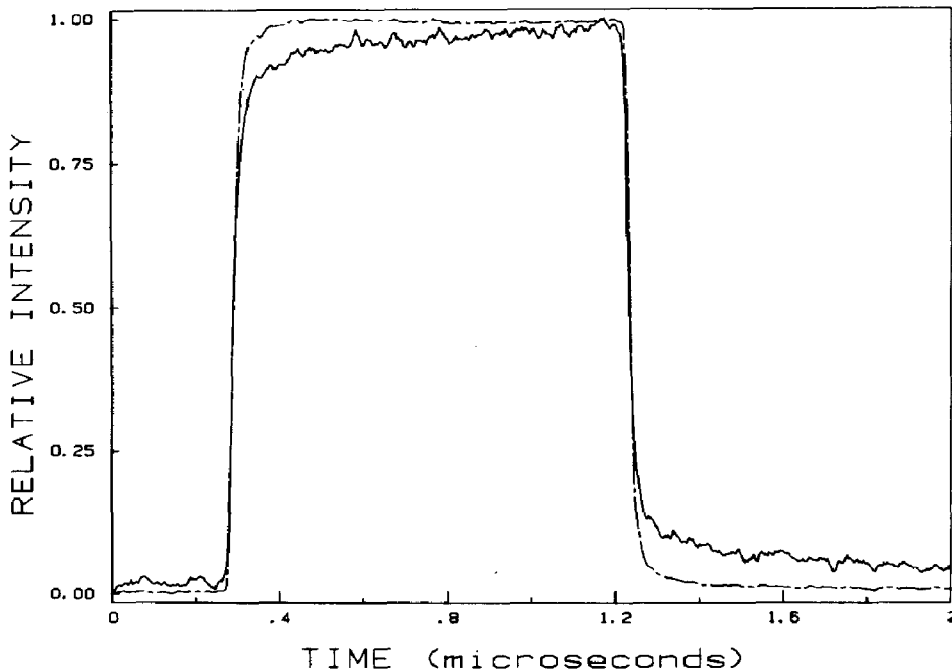


Fig. 5. Response of an Opto-Electronics element (1 mm^2) to an optical step function. When light is incident on the detector active area only (---), the rise and fall are limited by the AlGaAs optical driving pulse (about 15 ns). When a portion of the incident light falls on the non-active area (—), a second slower component appears. The intensity of the latter trace has been rescaled to facilitate comparison.

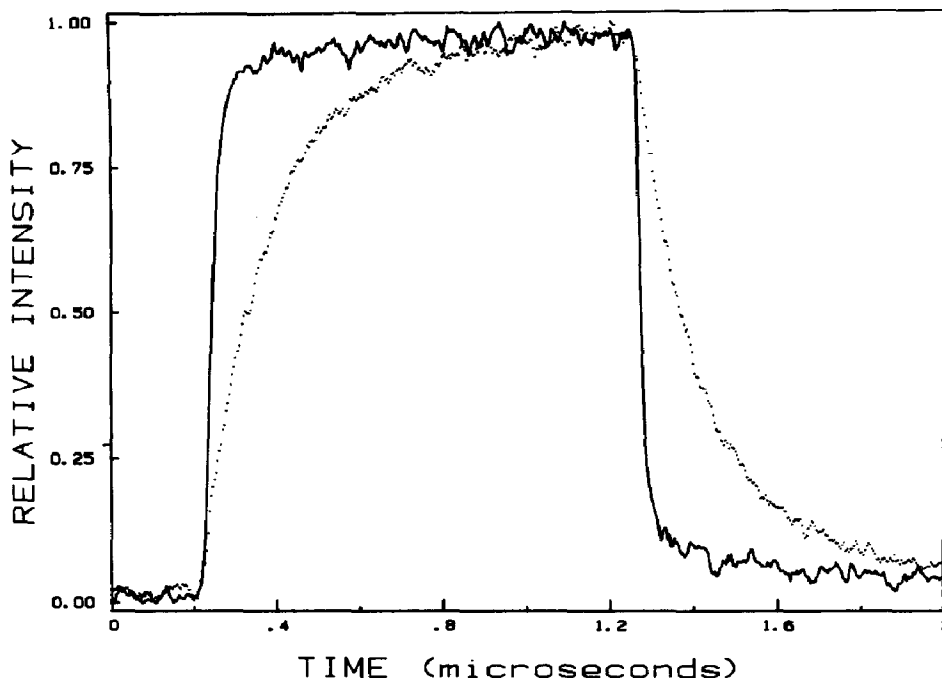


Fig. 6. Response of the Opto-Electronics (line) and the Judson (dots) 1 mm^2 germanium detectors to a $1 \mu\text{s}$ excitation pulse from an AlGaAs diode laser. The intensity of the latter trace has been rescaled to facilitate comparison.

The manufacturer's specifications for the respective elements indicate a peak responsivity of about 0.7 A W^{-1} (at about 1550 nm and 300 K) for each detector. Although it is difficult to quantify absolute signal intensities reliably and accurately under our experimental conditions, we are able to confirm, in a relative sense, that signal levels (responsivities) for the two detectors are indeed similar. In addition, noise levels in our system are determined principally by the buffer amplifier (see Section 2). Therefore, any attempt to calculate a detector NEP or D^* is a meaningless exercise. Despite similar responsivities, however, small differences in recorded intensities will exist since signal levels are extremely sensitive to the position of the fiber optic terminus relative to the germanium element. Consequently, we have normalized the signal intensities in order to facilitate comparison of the pulse profiles.

It is clear that for these particular elements under these particular conditions the Judson detector has a slower response than the Opto-Electronics detector. The rise and fall of the Opto-Electronics element is limited by the pulse used to drive the laser diode (about 15 ns). The slow component of detector response in the Opto-Electronics element was not as easily quantified as in the case of the Judson elements because it does not contribute as much to the total observed photocurrent. In terms of eqn. (1), this means that the pre-exponential factor A is much smaller for the Opto-Electronics

devices. Nevertheless, for the 1 mm^2 element in this particular circuit, the lifetime of the slow component on the rise and fall was determined to be about 550 ns. This number is suitable for use in a deconvolution routine [27]. At the limit of an 8 ns FWHM excitation pulse, it is quite difficult to see the slow component which again can lead to the incorrect conclusion that the entire detection system has a response time on the order of 15 ns (Fig. 7). (In fact, the system decay at this limit is more accurately represented as a convolution of the detector response with the Nd:YAG laser pulse. Consequently, a single exponential fit to the data is seen to be only an adequate representation of the detector response (Fig. 7).) Therefore, under our experimental conditions and for the specific elements examined in this study, the Opto-Electronics 1 mm^2 device is seen to give us the best response to a pulsed excitation source in which both active and non-active detector areas are illuminated. (An explanation of these facts begins to infringe on the proprietary right of Opto-Electronics, Inc. Nevertheless, a discussion of some points relevant in the construction of high speed junction devices is presented in refs. 21 and 22.) Although the detector response must still be deconvoluted from an observed signal, we are able to obtain kinetic information from a system that has a larger bandwidth.

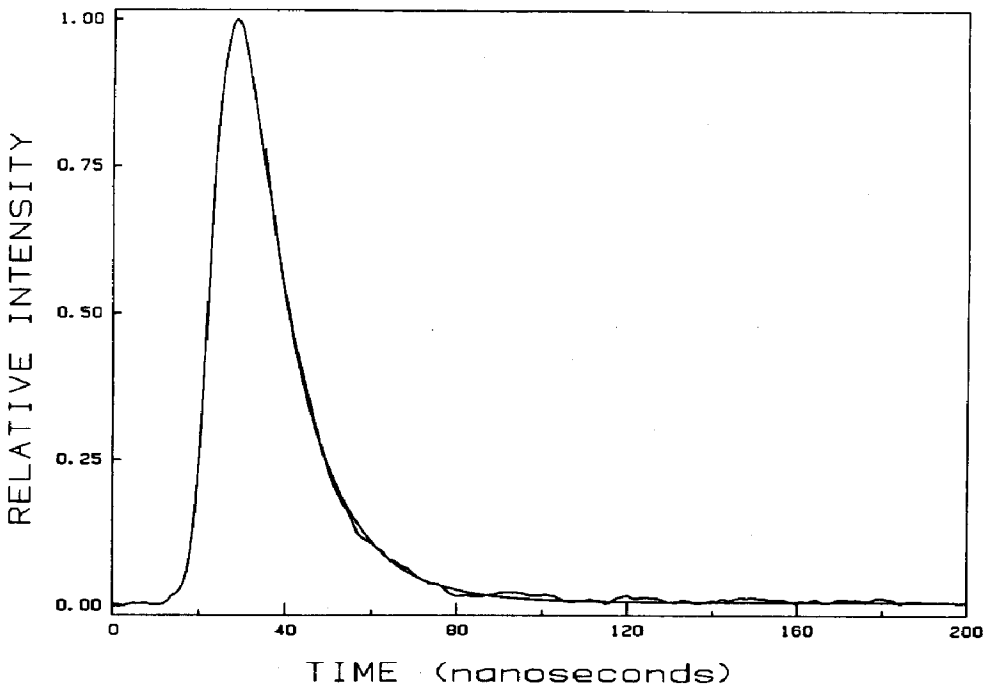


Fig. 7. Response of the 1 mm^2 Opto-Electronics detector to a 1060 nm 8 ns FWHM pulse (Nd:YAG laser).

4. Conclusion

We have examined several germanium p-n junction detectors under conditions that best approximate those in which $O_2(^1\Delta_g)$ serves as the excitation source. A self-imposed restriction in this study is that the detection system must be able to resolve nanosecond events. Consequently, RC limitations require the use of smaller detector elements. Since $O_2(^1\Delta_g)$ radiates into a sphere from a volume which is typically quite large (1 cm^3), it is difficult to collect a large percentage of the emitted photons and focus them onto an area smaller than 1 mm^2 . Consequently, charge carriers created in illuminated non-active areas of the germanium junction detector invariably contribute to the observed photocurrent. This gives rise to a detector response function that can interfere with the $O_2(^1\Delta_g)$ signal. Possible solutions to this problem include masking the non-active portions of the element, coupling the $O_2(^1\Delta_g)$ signal onto the active portion of the element with a fiber optic, and deconvoluting the detector response from the observed signal.

Acknowledgments

We would like to thank Mr. Fred Husher (University of New Mexico Chemistry Department electronics shop), for his assistance in the construction of our spectrometer. Helpful conversations with Dr. John P. Marton (Opto-Electronics, Inc.) and Ms. Susan Wells (Judson Infrared, Inc.) are acknowledged. This work is supported in part by grants from Research Corporation, the Sandia National Laboratories-University Research Program, and the National Science Foundation under grant number CHE-8501542. Acknowledgment is also made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

References

- 1 H. H. Wasserman and R. W. Murray (eds.), *Singlet Oxygen*, Academic Press, New York, 1979, and references cited therein.
- 2 A. A. Frimer (ed.), *Singlet Oxygen*, Vols. I - IV, CRC Press, Inc., Boca Raton, FL, 1985, and references cited therein.
- 3 K. I. Salokhiddinov, I. M. Byteva and B. M. Dzhagarov, *Opt. Spectrosc.*, *47* (1979) 487.
- 4 J. R. Hurst, J. D. McDonald and G. B. Schuster, *J. Am. Chem. Soc.*, *104* (1982) 2065.
- 5 J. G. Parker and W. D. Stanbro, *J. Am. Chem. Soc.*, *104* (1982) 2067.
- 6 P. R. Ogilby and C. S. Foote, *J. Am. Chem. Soc.*, *104* (1982) 2069.
- 7 M. A. J. Rodgers and P. T. Snowden, *J. Am. Chem. Soc.*, *104* (1982) 5541.
- 8 P. R. Ogilby and C. S. Foote, *J. Am. Chem. Soc.*, *105* (1983) 3423.
- 9 J. R. Hurst and G. B. Schuster, *J. Am. Chem. Soc.*, *105* (1983) 5756.
- 10 M. A. J. Rodgers, *J. Am. Chem. Soc.*, *105* (1983) 6201.

- 11 I. A. McLaren and R. P. Wayne, *J. Photochem.*, 16 (1981) 9.
- 12 J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley, New York, 1970.
J. B. Birks, *Organic Molecular Photophysics*, Vol. I (1973), Vol. II (1975), Wiley, New York.
- 13 B. Stevens, *Acc. Chem. Res.*, 6 (1973) 90, and references cited therein.
- 14 L. K. Patterson, G. Porter and M. R. Topp, *Chem. Phys. Lett.*, 7 (1970) 612.
- 15 G. Porter and M. R. Topp, *Proc. R. Soc. London Ser. A.*, 315 (1970) 163.
- 16 O. L. J. Gijzeman, F. Kaufman and G. Porter, *J. Chem. Soc., Faraday Trans. II*, 69 (1973) 708.
- 17 C. A. Burrus, A. G. Dentai and T. P. Lee, *Opt. Commun.*, 38 (1981) 124.
- 18 J. G. Parker and W. D. Stanbro, *Prog. Clinical Biol. Res. Ser.*, 170 (1984) 259 - 284.
J. G. Parker and W. D. Stanbro, *J. Photochem.*, 25 (1984) 545.
- 19 S. M. Sze, *Semiconductor Devices: Physics and Technology*, Wiley, New York, 1985.
- 20 B. G. Streetman, *Solid State Electronic Devices*, Prentice Hall, Englewood Cliffs, 1972.
- 21 B. K. Garside and F. L. Gouin, *Proc. Soc. Photo-opt. Instrum. Eng.*, 355 (1982) 27.
- 22 L. A. Godfrey, *Opt. Spectra*, 13 (1979) 43.
- 23 G. Lucovsky and R. B. Emmons, *Appl. Opt.*, 4 (1965) 697.
- 24 D. Long, in R. J. Keyes (ed.), *Topics in Applied Physics*, Vol. 19, *Optical and Infrared Detectors*, Springer, Berlin, 1980, pp. 101 - 147.
- 25 W. Budde, in F. Grum and C. J. Bartleson (eds.), *Optical Radiation Measurements*, Vol. 4, *Physical Detectors of Optical Radiation*, Academic Press, New York, 1983, pp. 232 - 277.
- 26 C. E. Hurwitz, *Opt. Eng.*, 20 (1981) 658.
- 27 K.-K. Iu and P. R. Ogilby, *J. Phys. Chem.*, in the press.
- 28 A. Grinvald and I. Z. Steinberg, *Anal. Biochem.*, 59 (1974) 583.
A. Grinvald, *Anal. Biochem.*, 75 (1976) 260.
- 29 J. N. Demas, *Excited State Lifetime Measurements*, Academic Press, New York, 1983.
- 30 P. A. Jansson, *Deconvolution*, Academic Press, New York, 1984.
- 31 P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences*, McGraw-Hill, New York, 1969.