Photothermal spectroscopy

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incident radiation is not attenuated by absorbers, there is no inner-filter effect and the measured emission intensity is directly proportional to analyte concentration over an extended range. Although the sensitivity of the method is normally less than that for one-photon excitation, experience has shown that in optically dense matrices, the detection limits can quite often be better. This fact is due to the extremely large scatter blank normally present in single monochromator instruments when front-surface excitation is employed. Because of the large separation of excitation and emission wavelengths and the ability to use a right angle configuration, the blank for two-photon excitation is generally dark current limited. Another advantage of two-photon excitation in absorbing matrices is the ablity to bulk excite the sample. Front surface methods risk interference from fluorophors adsorbed onto the cell wall or emission from the cuvette itself. Also, the bulk excitation capability is highly important for solid state analyses where the surface concentration may not be representative of the entire sample.

The synchronously-pumped laser has not, to our knowledge, been reported as a source for two-photon spectroscopy. The possible range of wavelengths with an argon-ion pump laser extends from 420–690 nm, allowing study of a wide variety of molecular systems. Cavity-dumped operation grants additional flexibility in making the system well suited to time-resolved spectroscopy and synchronous photon counting (3). Problems common to other pulsed dye laser sources are substantial pulse height variations and large, potentially destructive, beam energies. The synchronously-pumped laser, however, is characterized by excellent pulse-to-pulse reproducibility via mode-locking. The picosecond duration allows peak powers sufficiently large to induce two-photon absorption, yet maintains the beam energy at levels sufficiently low to avoid thermal effects in the sample. Finally, because of the scarcity of continuously tunable ultraviolet sources, it is advantageous that two-photon excitation accesses states in this region while minimizing problems with photolytic degradation of the sample.

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Photothermal Spectroscopy

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Photothermal spectroscopy (PTS) involves the use of thermistors in contact with the sample to determine the spectral response of highly absorbing samples. The technique was evaluated with crystalline solids (CdS and TiO_2) and solutions of the dyes rose bengal, methylene blue, and aniline yellow. The instrumental and cell designs suitable for solid and liquid samples are described and suggestions are made for further improvements in the techniques.

There has been much recent interest in the use of thermal detection techniques for the spectroscopic examination of different types of samples (1–6). For example, photoacoustic spectroscopy (PAS) (1–4) involves the detection with a sensitive microphone of the pressure fluctuations in a gas arising from heat produced by the absorption of radiation from a modulated light beam. This technique has the advantage of not requiring optical detection of transmitted or reflected light, and it can be applied to samples which are difficult to examine by conventional spectroscopic methods. Thermal detection methods also have been suggested for the determination of absolute quantum yields by employing calorimetric techniques which are free from the geometrical correction problems of optical methods (5–8). These have also frequently employed microphone detectors (6, 8) or the monitoring of volume expansion (7).

While PAS and related techniques have been used quite successfully, they require sample placement in sealed cells and utilize rather expensive, highly sensitive microphones which can be troubled by external acoustic noise. Moreover, PAS has, so far, not proved useful for spectroscopic studies of the solid/liquid interface. We thought it worthwhile to investigate the direct detection of the temperature changes resulting from radiationless processes occurring following light absorption, using a thermistor detector during irradiation of the sample with a high intensity source. Thermistors have been employed extensively for calorimetric and analytical measurements, such as thermometric titrations (9, 10). They have also found application to studies of electrode reactions (11–13) and for enzyme reactions at electrode surfaces (14).

The technique we propose, photothermal spectroscopy (PTS), involves placing a thermistor in close proximity to the sample (solid or liquid) and measuring temperature changes (i.e., thermistor resistance changes) during sample irradiation with high intensity monochromatic light. This technique is similar to PAS, in that the radiationless processes following light absorption are detected, but it allows a more flexible sample cell arrangement and is free of acoustic noise problems. PTS should be especially sensitive for samples of high molar absorptivity (ϵ) such as solids or optically dense liquids, where a large fraction of the impinging radiation is absorbed. PTS
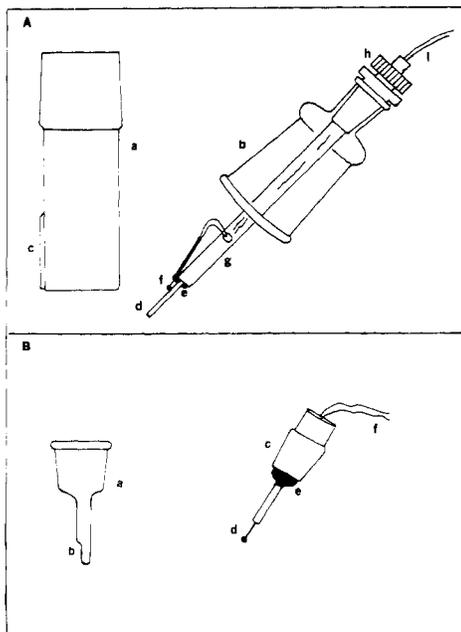
Figure 1. (A) Cell used for crystals or solid samples. (a) Body of cell with 40/50 male connection. (b) Top of cell with 40/50 female connection. (c) Optical flat (quartz). (d) Crystal or solid sample. (e) Epoxy cement holding sample and thermistor in place. (f) Thermistor. (g) Glass tube. (h) Teflon thermometer adapter 14/30. (i) Thermistor leads. (B) Cell used for solutions. (a) Body of cell (quartz) with 12/18 female connection. (b) Flat area for irradiation. (c) Top of cell which holds thermistor probe. (d) Thermistor, silver coated. (e) Silicone rubber cement. (f) Thermistor leads

Figure 2. Block diagram of PTS system. See text for details

Figure 3. Comparison between the power spectrum of the xenon lamp taken with the radiometer and the photothermal spectra of carbon black. (●) PTS using height of heating curves. (△) PTS using integral weight of heating curves. (□) radiometer response

thus complements optical measurements of absorbance in more dilute samples and, since it does not detect radiation directly, it is not affected by scattered or stray light problems of reflectance methods. We report here measurements on several solid and liquid samples using a simple PTS apparatus. Future papers will describe more advanced instrumentation and discuss the theory of PTS.

EXPERIMENTAL

Apparatus. A basic description of the PTS experiment is as follows. The thermistor probe is placed within, on, or near the sample, preferably out of the path of the high intensity monochromatic irradiation light. A fraction of the light absorbed is converted to heat which reaches the thermistor by thermal diffusion. The temperature change results in a change of resistance in the thermistor, causing an unbalance in a Wheatstone bridge in which the thermistor forms one arm. The resulting voltage change is detected with an electrometer, amplified and displayed.

The cells used for thermal absorption measurements are shown in Figure 1. Both cells are equipped with optical flats for irradiation purposes and a thermistor for detecting temperature changes following the absorption of radiation. For most of the experiments, the thermistors were from Victory Engineering Co. (Model 32A223), and had a nominal resistance of 2 kΩ, a sensitivity of 78 Ω/K, and a time constant of 0.4 s in still water. Since the thermistor is black, direct absorption of light energy by it is a problem during measurements in solution. To minimize this effect, a reflective silver coating was prepared for the thermistor by using electrodeless deposition with a silver nitrate–glucose mixture. This coating decreases the direct photoeffect to approximately 1% of the original value but still permitted heat conduction to the thermistor. When the PTS of crystals was investigated, the thermistor was not directly in the light path. In this case the thermistor was fixed on the upper portion of the transparent crystal with silicone adhesive. Then the light was permitted to strike only the lower portion of the crystal (Figure 1). Similar techniques were used to measure the spectrum of both thin film and powdered CdS samples. For thin film experiments, CdS was vacuum-evaporated onto a thin glass plate and then
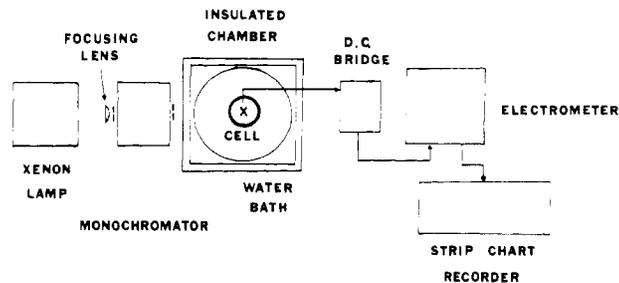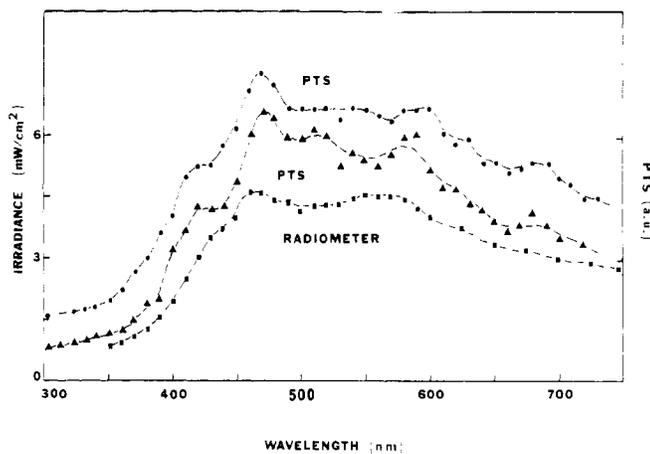
mounted in the cell like the crystals. The spectrum of the semiconductor powder (CdS) was obtained by applying silver epoxy to one side of a brass sheet and the powder was then added on top of the wet epoxy. In this case the brass sheet was mounted and the thermistor placed on the rear portion opposite the CdS powder.

The instrumentation used for these experiments is shown in Figure 2. The light source was a Hanovia 2.5-kW short arc xenon lamp housed in an Oriel Model LH-152N housing. The light beam was focused using a $f/1$ quartz lens through a Jarrell-Ash Model 82-410 Monochromator. The fixed slits used were of about 7-nm band pass. The cell was placed in an unthermostated water bath which was inside an insulated box. The entire chamber was then positioned for maximum irradiation of the cell. The spectral distribution of the lamp was measured with an EG & G Radiometer/Photometer, Model 550-1 passing the light first through an Oriel neutral density filter (0.50 absorbance). When the 7-nm band pass slits were used, the lamp was found to have an average intensity of 2.3 mW/cm² from 400–750 nm. The actual lamp power spectrum is given in Figure 3. The thermistor was one arm of a Wheatstone bridge powered by a dc source of 1.35 V. The voltage from the bridge was measured with a Keithley Model 600A electrometer and displayed on a Moseley Model 7100B strip chart recorder. The sensitivity was such that a 0.0017 °C temperature change resulted in an unbalance voltage at the bridge of 3.5×10^{-5} V; this was amplified 3300 times, and resulted in a 1-inch deflection on the recorder. Data was obtained point-by-point at each wavelength as described in the procedure section.

A few experiments employed a faster transistor (Victory P85B10 with a time constant of 7 ms in water). In this case the light beam was chopped at 12 Hz and the signal detected with a PAR Model 122 (Princeton Applied Research Corp.) phase sensitive detector. In this case the spectrum was scanned slowly and the output recorded on an $X-Y$ recorder. A Cary Model 14 spectrophotometer was employed for all absorption measurements.

Chemicals. The soluble dyes: methylene blue (MB) (Fisher), aniline yellow (AY) (Allied Chemical), and rose bengal (RB) (Eastman) were all of technical grade and used without further purification. Titanium dioxide was a single crystal in rutile form
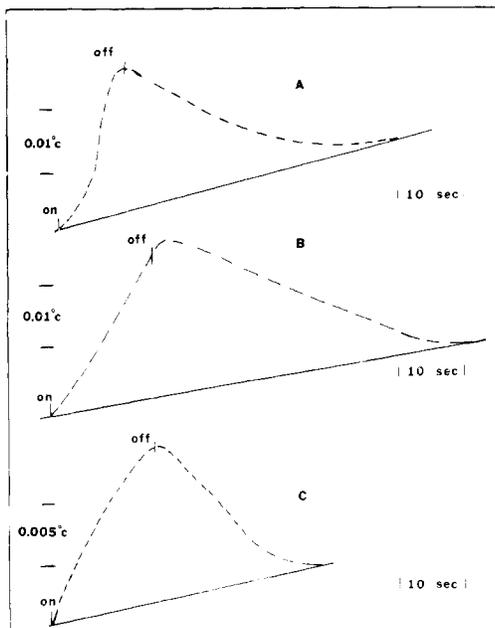
Figure 4. Comparison between representative response curves for solid and liquid samples. All curves were taken at a wavelength where the sample is strongly absorbing. (A) Carbon black pellet (460 nm). (B) CdS single crystal (510 nm). (C) Methylene blue solution 0.33 g/L (625 nm)

and was obtained from Nakazumi Crystal Co., Ltd. The cadmium sulfide single crystal was obtained from Teikoku Tsushin Kogyo Co. Ltd. Both crystals were about 1 mm thick with irradiated surface areas of 0.7 cm². The crystals were prepared first by sanding with abrasive paper and then polished until transparent with polishing alumina (0.3 μm). CdS powder was commercially obtained. The CdS thin film was deposited on a glass sheet by vacuum evaporation of CdS powder at about 10^{-5} mm Hg for 10 min. The thickness of the film depended upon the evaporation time. The film used was about 1–1.5 μm in thickness.

Procedure. In a typical experiment the thermistor was reproducibly positioned in the cell. Then the cell itself was placed in the water bath and permitted to equilibrate. After the bridge signal became steady, the photothermal spectrum was taken point-by-point at 5, 10, or 25 nm intervals. At each wavelength the light was permitted to irradiate the cell for a given time, e.g., 15 s. Then the light was blocked with a shutter and the cooling curve was recorded until the heat was dissipated from the cell. Typical response curves for different samples are shown in Figure 4. The maximum heights of the response curves were measured and corrected for the intensity of light at each wavelength. When the curves were integrated, the photothermal spectrum had the same shape, and higher sensitivity with less scatter of data points.

RESULTS AND DISCUSSION

PTS of Carbon Black. To evaluate the system, carbon black was chosen as the standard sample. Since this sample approaches an ideal black body, it will absorb all wavelengths so that the emitted heat is large and easy to measure. Thus, the photothermal spectrum of carbon black should be the same as the output power spectrum of the xenon lamp and monochromator. The experiment was carried out by placing the thermistor inside a carbon black pellet which was then mounted and placed in the cell as shown in Figure 1a. Then the spectrum was obtained, from response curves obtained at 10- or 25-nm intervals. A typical response curve at 460 nm is shown in Figure 4a. When the light was permitted to strike the pellet, there was a small transient and then heating during the light-on pulse was observed. The temperature increase was very large and easily measured. The rising base line can be attributed to small changes in room and bath temperatures, mainly caused by heating from the xenon lamp and power supply. The resulting spectra are shown in Figure 3. The

upper curve was obtained by measuring the heights of the individual response curves, while the middle curve shows the integrals of each response curve. These (in arbitrary units) are compared to the corrected spectral distribution of the lamp obtained with the radiometer (in mW/cm²). All three curves are very similar and have the reported general characteristics of a xenon lamp (15). The signal-to-noise ratios of the PTS curves were very dependent upon the particular thermistor employed. In some cases a thermistor had to be discarded because of noise problems.

These spectroscopic results on carbon black are similar to those obtained by PAS (1–4). This simple PTS method might be useful for determining the spectral distributions of reasonably intense sources.

Semiconductor Materials. There has been much interest in the use of semiconductors in solar energy research. An important parameter of semiconductors is the band-gap energies (E_g), which is usually measured spectrophotometrically by absorption or reflection techniques. For absorption measurements, the crystal must be polished extremely well in order to minimize scattering and must be sufficiently thin to have a reasonable transmittance. Reflection measurements are particularly troubled by light-scattering effects and both methods are inconvenient for polycrystalline samples.

A typical response curve of a transparent cadmium sulfide single crystal taken at 510 nm is shown in Figure 4b. The thermistor was attached to the upper front of the crystal and the light impinged only on the lower portion. In this case the response time was short, and the temperature still increased after the light beam was blocked and then gradually decreased. We found the time response behavior depended on the place of the thermistor. If the thermistor was fixed in another position, for example, at the upper rear of the crystal, a relatively large time delay was seen when the lamp was turned on. This can be attributed to the time needed for the heat produced at the point of irradiation to thermally diffuse to the thermistor. The thermal absorption spectra of single crystalline CdS and TiO_2 are compared to their respective absorption spectra in Figure 5. Note that the optical absorption spectra do not limit in the band–band excitation region while, in the photothermal spectrum, the response attains a limiting value in the band–band excitation region. We also tried to measure PTS of very thin vapor deposited films and nontransparent materials (polycrystals or powders). Figures 6 and 7 show PTS of a vacuum deposited film of CdS and that of CdS powder, respectively. The ability to measure easily the band-gaps of semiconductors even when they are immersed in solution, as well as their general spectral behavior, is a significant application of PTS.

PTS of Solutions. PTS was also applied to solutions of various organic dyes. To make thermal measurements in solution, the thermistor was silver-coated to minimize photoeffects of the thermistor itself. Several other methods were also used in an attempt to decrease this blank effect of the thermistor, including beam stops and white reflective paint (i.e., of titanium dioxide) still produced a small background response curve when the thermistor was irradiated in the nonabsorbing solvent. Since a 100% reflective coating could not be obtained, the photothermal spectra for solutions had to be corrected for this background effect. This was accomplished by first doing PTS of the solvent alone. The spectra obtained of the solvents had the same shape as the lamp-monochromator power spectrum but were of a much smaller magnitude than those observed with carbon black. The PTS signal size was inversely proportional to the specific heat of the solvent (16). A similar effect was also seen in PAS studies of solutions by Adams et al. (3). This effect was minimized by placing the thermistor inside the solution against
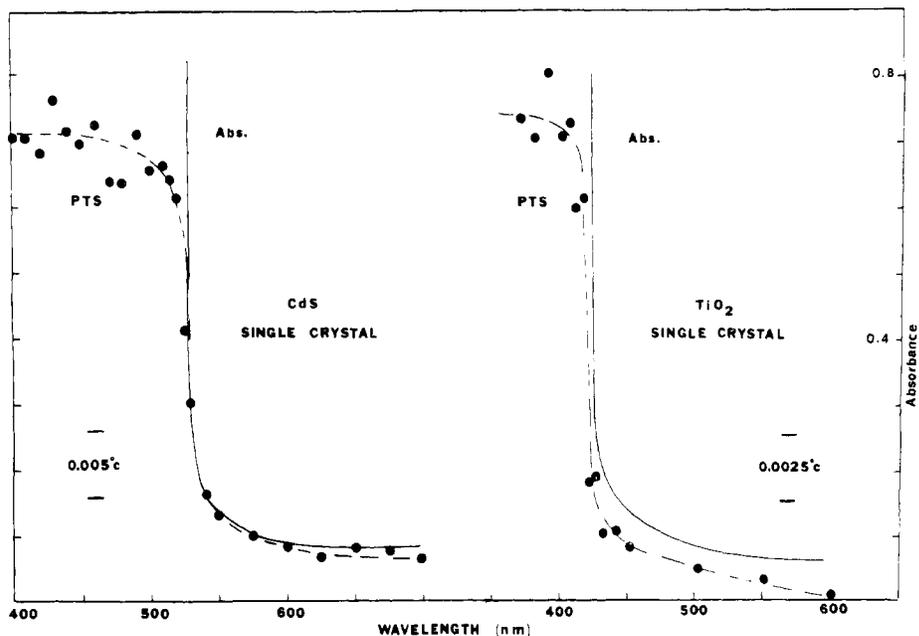
Figure 5. Comparison between photothermal spectra and optical absorption spectra of two semiconductor single crystals. CdS – E_g = 2.4 eV, TiO₂ – E_g = 3.0 eV
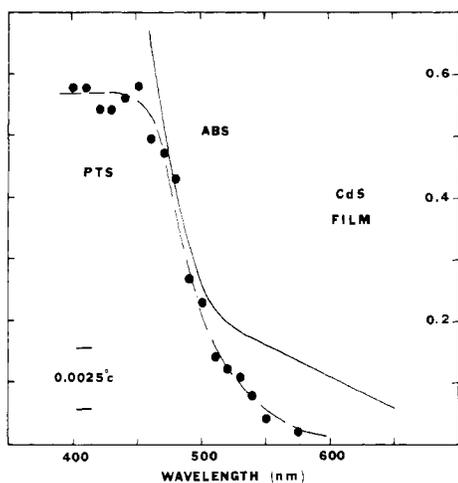
Figure 6. Photothermal spectrum of CdS vacuum evaporated film. Solid line shows the absorption spectra
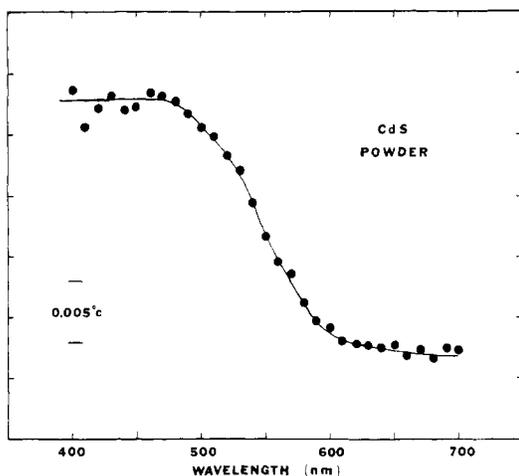
Figure 7. Photothermal spectra of CdS powder on brass

the glass cell wall closest to the lamp. Under these conditions the background effect would not vary very much when the

absorbing sample was added to the solution. All of the results were corrected for the background by running a blank in solvent alone before addition of dye and were also corrected for the spectral distribution of the xenon lamp.

The dyes used are very strong absorbers (i.e., have large molar absorptivities): rose bengal (λ_{max} 547, $\epsilon \approx$ 130 000), methylene blue (λ_{max} 655, $\epsilon \approx$ 89 000) and aniline yellow (λ_{max} 384, $\epsilon \approx$ 25 000) (17, 18). A typical response curve of MB taken at 625 nm is shown in Figure 4a. When the light was turned on, heating occurred almost immediately, because the light could strike the solution which was directly in contact with the thermistor. When the light was turned off, the cooling was very rapid, because the water has a large heat capacity and can dissipate the heat near the thermistor easily. This curve is representative of all dye solutions near λ_{max} of the dye.

The photothermal spectra of rose bengal is shown and compared to its respective absorption spectra in Figure 8. Although these solution PTS curves show general absorption peaks in the vicinity of the spectrophotometric absorption maxima, they are far from quantitatively correct. Also shown in Figure 8c is a corrected directly recorded curve using the thermistor with the faster response, with the light chopped at 12 Hz and phase-sensitive detection. The results again are not very satisfactory. Several factors lead to these difficulties in the PTS of solutions; the need to correct for both the source spectral distribution and the thermistor response in blank solution leads to major differences in the temperature rise measured and that ultimately plotted. Moreover, since PTS is a function of both the optical and thermal characteristics of the sample, the blank correction method is valid only for optically dilute solutions. The temperature change sensed by the thermistor represents the heat evolved during the light-on period in a volume of solution surrounding the thermistor determined by the thermal diffusion length. For optically dense solutions, although more radiation may be absorbed, this occurs near the front window of the cell and relatively less heat will be detected by the thermistor. This same effect will cause problems in the intercomparison of solutions of different concentrations, as is evident from the results in Figure 8, even with the thermistor placed near the front window of the cell.
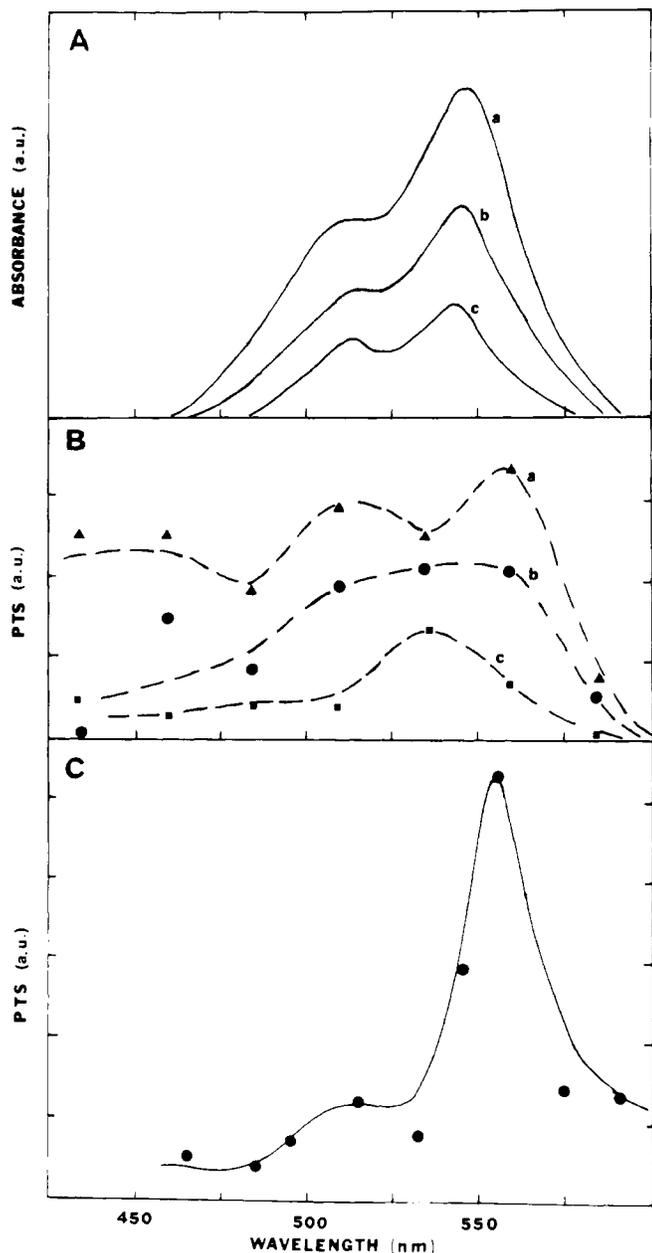
Figure 8. Comparison between optical absorption spectrum and photothermal spectra of rose bengal in solution. (A) Optical absorption spectrum, (a) 1.0 g/L, (b) 0.1 g/L, (c) 0.02 g/L. (B) PTS using integral weight of individual heating curves. (a, b, c) same as in A. (C) PTS using phase sensitive detection and fast thermistor on rose bengal adsorbed on the thermistor

Simplified Theory of PTS. The simplest case to consider in PTS is one in which the thermal conductivity of the sample is so large that its temperature remains uniform throughout and the sample is immersed in a bath of uniform and constant temperature, T_b. Assume a beam of monochromatic light with an intensity I_0 (cal·s^{-1}· cm^{-2}) and area A impinging on the sample of density, ρ_s, volume, V_s, specific heat, C_s, and total surface area in contact with the bath, A_s. If the coefficient of light absorption of the sample at this wave length is β and the sample thickness where the beam is incident is l, then the total rate of heat absorption by the sample is

$$\text{heat absorption (cal·s}^{-1}) = I_0(1 - e^{-\beta l})A \qquad (1)$$

If the sample can fluoresce, this expression would have to be modified by terms which depend upon the fluorescence efficiency and portion of the impinging light being converted

to heat by vibrational relaxation within a given electronic state. For a liquid, $\beta = 2.3 \, \epsilon C$, where ϵ is the molar absorptivity and C is the concentration.

The rate of heat dissipation to the bath surrounding the sample is generally taken as (19)

$$\text{heat dissipation (cal·s}^{-1}) = H(T - T_b)A_s \qquad (2)$$

where T is the sample temperature and H is the coefficient of surface heat transfer (cal·s^{-1}·cm^{-2}·°C^{-1}). When light of intensity I_0, impinges on the sample from time, $t = 0$ to τ (at which time the light is turned off), the change of sample temperature with time is given by:

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{I_0(1 - e^{-\beta l})A - H(T - T_b)A_s}{\rho_s V_s C_s} \qquad 0 \leqslant t \leqslant \tau \quad (3)$$

Letting a, the absorption parameter be given by

$$a = I_0 A(1 - e^{-\beta l})/\rho_s V_s C_s \qquad (4)$$

and b, the dissipation parameter be

$$b = HA_s/\rho_s V_s C_s \qquad (5)$$

then the equations governing the behavior can be written

$$\mathrm{d}T/\mathrm{d}t = a - b(T - T_b) \qquad 0 \leqslant t \leqslant \tau \qquad (6)$$

$$\mathrm{d}T/\mathrm{d}t = -b(T - T_b) \qquad t > \tau \qquad (7)$$

with the initial condition, $t = 0$, $T = T_b$.
Solution of these equations yields

$$(T - T_b) = (a/b)(1 - e^{-bt}) \qquad 0 \leqslant t \leqslant \tau \qquad (8)$$

$$(T - T_b) = (a/b)(1 - e^{-b\tau})e^{-bt} \qquad t > \tau \qquad (9)$$

These are the simplified equations for the PTS response curves, assuming the response time of the thermistor is very small compared to τ. The dependence of the response on wavelength and intensity is contained in the factors β and I_0 contained in a.

Some limiting cases are of interest. When there is no heat dissipation to the bath, $H = 0$, $b = 0$, and

$$T - T_b = at \qquad 0 < t < \tau \qquad (10)$$

$$T - T_b = a\tau \qquad t > \tau \qquad (11)$$

In this case the temperature will increase linearly during the irradiation and remain constant during the dark period. When dissipation is present, the rate of temperature increase will be slower (eventually attaining a steady state value, $T - T_b = a/b$) and the temperature will decay exponentially in the dark. The maximum temperature attained and the integrated areas will be proportional to a under all conditions. The variation of a with wavelength, and hence the shape of the PTS spectrum, will depend upon the magnitude of βl. Two limiting cases can be considered. When βl is large (e.g., >3), $(1 - e^{-\beta l}) \approx 1$, $a = I_0 A/\rho_s V_s C_v$; thus a is independent of wavelength. This represents the saturation condition where all of the light energy is absorbed by the sample independent of the wavelength. This is the response observed in carbon black and at wavelengths with energies above the band gap energies in the semiconductors. When βl is small (e.g., <0.1), $(1 - e^{-\beta l}) \approx \beta l$, $a = I_0 A\beta l/\rho_s V_s C_v$, and the response follows the absorption curve.

The actual response in PTS is considerably more complex than the treatment given above, since the temperature distributions in the sample and the bath (which depend upon the thermal conductivities of the media), as well as the location and the response time of the thermistor, must be taken into account. This involves solution of the partial differential equations for heat conduction for the appropriate geometries and boundary conditions (19).

CONCLUSIONS

The results show that, even with this relatively simple approach, satisfactory results can be obtained with solid samples. Thus PTS is a simple method of obtaining the band-gap energy of semiconductors and has recently also proved useful in studying the spectral and electrical potential dependence of the temperature of a semiconductor electrode under irradiation (20). This latter application may be especially useful, since few methods exist for studying the spectroscopy of an operating electrode in situ. Improvements in cell design, apparatus, and instrumentation are possible and these would improve the response and make the treatment of the data more convenient. The addition of a well-controlled thermostat bath around the sample would decrease base-line corrections. Similarly the use of a matched pair of thermistors in a differential arrangement, both in contact with the samples but one near the irradiated portion and one in the dark, could be employed. This idea has already been applied and the base-line drift has almost completely been eliminated even in an unthermostated bath. With this arrangement it might also be possible to construct a dual-beam instrument for direct correction of the spectral output of the lamp–monochromator system. The PTS of solutions would be improved by finding a better reflective, but thermally conducting, coating for the thermistor which would decrease its background response. Such improvements, as well as further applications and a theoretical treatment of PTS are currently being investigated.

ACKNOWLEDGMENT

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Nonlinear Calibration

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This paper deals with the problem of finding the statistical uncertainty expressed as confidence limits for an analysis based on a measurement and read through a nonlinear calibration or standard curve of arbitrary form. Several alternative methods with varying levels of computational complexity are proposed and an illustrative example shows the results obtainable by each method.

A recent publication (1) has noted that when an analysis X is determined by reading a measurement Y through a nonlinear calibration curve, the probability distribution of X cannot be expected to be normal (Gaussian) even though the random scatter of Y is distributed normally. Consequently, the use of the statistics "mean" and "standard deviation" to describe the location and uncertainty, respectively, of X is somewhat problematical as these measures apply unambiguously only to the normal distribution. In fact, the mean of replicate measurements of Y, which is the unbiased best estimate of the true Y value, when projected through the calibration curve, yields the mode of the X distribution function. This X value, although the best estimate of the true value of the analysis, deviates from the mean of the X distribution function as sketched in Figure 1 of Ref. 1. The

purpose of this study is to explore the use of the statistic "confidence interval" (between two "confidence limits") as a more appropriate measure of the uncertainty of the non-normal random variable X. This notion is not new having been discussed long ago in connection with analyses projected through linear calibration lines (2–4). Later, the method was extended to situations involving measurements of several different samples where simultaneous or joint confidence intervals are required for all the corresponding analyses as read through a common linear calibration line (5–7). The further extension to nonlinear calibration curves, although cited formally by Miller (7), apparently has not been discussed in a practical way in the chemical literature.

The problem is formulated as follows: Calibrating measurements y_i are taken of a series numbering n standard known samples x_i. One or more measurement of y_i may be made of each x_i. The number of replications of each y_i is denoted as n_i. These data are used to construct a calibration curve $y_{cal}(x)$ to represent the unknown functional dependence $y(x)$, which is in general nonlinear. A number N of unknown samples similar in nature to the calibrating samples are to be analyzed for the quantity X by measurement of Y in a manner identical to the calibrating measurements. N_i replicate Y_i measurements may be made, and corresponding X_i values are determined by projecting Y_i through the calibration curve.