RAPID SCAN SPECTROMETRY
application notes

Analytical Instruments
Number 9

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LUMINESCENCE MEASUREMENTS WITH THE TEKTRONIX J20/7J20 RAPID SCAN SPECTROMETER

The TEKTRONIX J20/7J20 is a rapid-scanning spectrometer (RSS) which employs as an integral unit, a monochromator and a unique imaging detector which can offer a spectroscopist some heretofore very difficult measurement capabilities. The TEKTRONIX RSS offers a trade-off of sensitivity and time resolution at the desire of the operator, something unavailable until now in a rapid-scanning spectrometer.

The TEKTRONIX RSS (Figure 1) has the capability of performing virtually any spectral measurement associated with ultraviolet, visible, near-infrared luminescence. The general term "luminescence" describes any emission of light (not necessarily visible) from any source. This discussion concerns itself with the luminescence associated with fluorescence and phosphorescence in chemical, biological, and physical systems of interest. These luminescences span the full ranges of intensities, spectral regions, spectral shapes, and lifetimes of decay. The TEKTRONIX spectrometer system can detect a significant proportion of these luminescent phenomena.

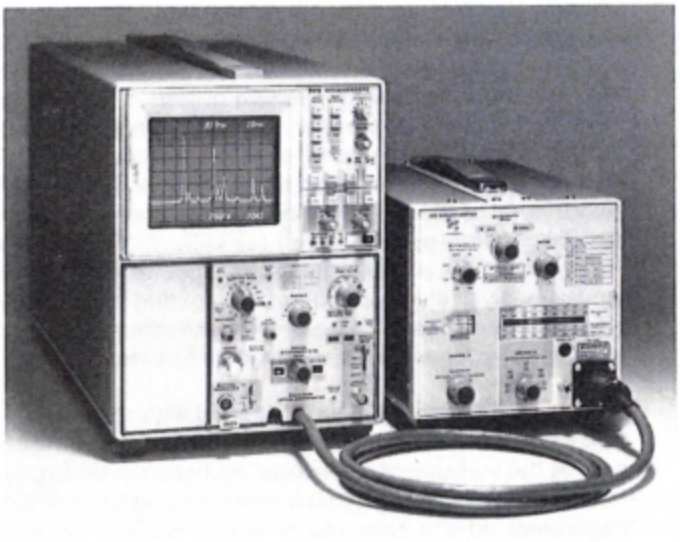


Fig. 1. The TEKTRONIX J20/7J20 Rapid Scan Spectrometer System.

Molecular Luminescence

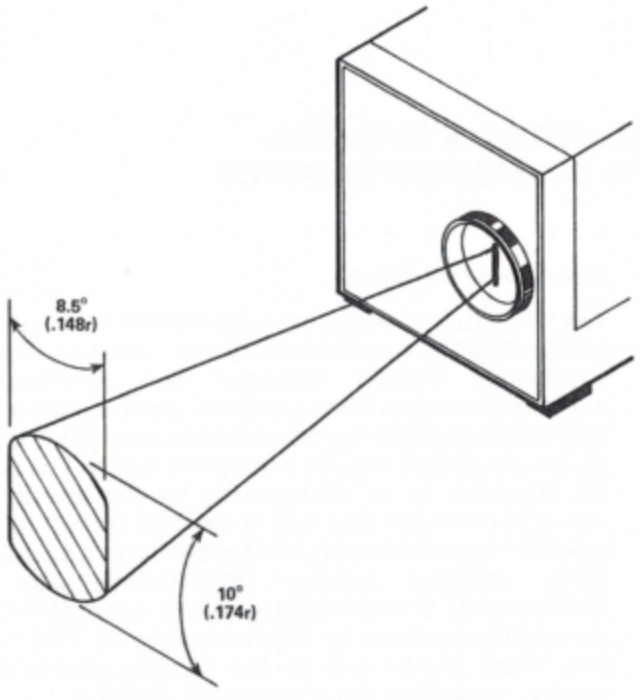
The two types of molecular luminescence most often encountered are fluorescence and phosphorescence. For large unsaturated organic molecules and transition-metal molecules and ions, these emissions generally occur in the ultraviolet and visible regions with a few occurring in the near IR. We are dealing with the emission of light as the result of the relaxation of an electronically excited species. The means of excitation may vary. It could be the result of light irradiation (luminescence), electric discharge (plasma emission), chemical reaction (chemiluminescence, bioluminescence, or electroluminescence), or physical stimuli (thermoluminescence or triboluminescence). The spectra from these sources can be line spectra, broadened line spectra, unresolved band spectra, or continua. The quantities of interest are wavelength of spectral peaks or features, intensities, overall shape, separation of peaks, and decay characteristics. The J20/7J20 rapid-scanning spectrometer can measure these quantities provided there is a spectral flux of at least 5 pW of spectroradiant power entering the effective aperture of the spectrometer.

Typical Measurement Situations

Generally, luminescence is measured from an extended source. As an example, let us consider a phosphorescence. The sample is often about 1 cm by 2 or 3 cm. The emission emanates from a rather large volume. In order to record the spectrum of this light, it must be focused on the aperture of the instrument. A lens can be used but its f-number should be the same as the equivalent f-number for the J20 Spectrometer (i.e., f/6.0). All external optics for focusing the sample onto the entrance slit, including any mirrors used to reflect the luminescence back on itself, should be f/6.0. The image-to-object size ratio should be optimized so that the image is very nearly the size of the entrance slit aperture of the J20 Spectrometer. The entrance slit height is 7 mm with widths selectable from 10 μm to 1000 μm in 1:2:5 steps.

Another method, if there are no physical limitations, is to position the luminescent sample as close to the entrance slit as necessary for the emitting volume to fill the instrument

acceptance angles completely. (See Figure 2.) A back-reflecting mirror can be used to gather more of the light, and it should be f/6.0. The entrance slit should be chosen to provide sufficient resolution to yield an accurate spectrum, but no narrower. This usually consists of selecting narrower and narrower entrance slit widths until no further sharpening of the spectrum occurs.



PROJECTION AND APPROXIMATE SHAPE
OF THE INSTRUMENT STERADIANCY

Fig. 2. Steradiancy projection of the J20 showing acceptance angles and approximate shape of detected area on a surface normal to the optical axis.

The instrument contains two gratings, back-to-back, which are selectable by a knob on the J20 Spectrometer. Grating A provides a display of 400 nm and a resolution of 4 nm, and Grating B provides a 40-nm display with 0.4-nm resolution. For most molecular electronic spectra, Grating A will be most useful, providing a display of the complete emission envelope with sufficient resolution for samples in condensed media at liquid-nitrogen temperatures. This grating is steppable in 100-nm steps to cover the 1100-nm window. The B grating is continuously variable over the full range of the instrument. The ultraviolet is accessible in second order (from below 250 to 300 nm) by the use of a UV-pass filter which is built into the instrument and can be selected if desired. 400-nm and 500-nm UV cutoff filters are also provided to sort out the various orders. The spectral bandwidth of the instrument varies with the entrance slit width selected down to 100 μm. Below this point, the vidicon detector begins to become the limiting factor in resolution. Decreasing the entrance slit width further will increase the resolution to a degree but not linearly. To get radiometric power readings of lines narrower than the spectral bandwidth of the instrument, it is necessary to integrate the spectral peaks.

The spectrometer can be used in either a radiometrically calibrated mode, or in an uncorrected mode. If the spectra are recorded in the corrected mode, the spectral response of the system will be made effectively flat. In the uncorrected mode, the system spectral response will be increased. In the corrected mode, the system is calibrated to measure *radiance*, i.e., the amount of spectroradiometric power entering the spectrometer per unit solid angle per unit aperture area. The units of this quantity are watts nm^{-1} $steradian^{-1}$ cm^{-2}. In the CRT readout of this quantity, the steradiancy of the instrument and the slit areas are taken into account yielding the net units of watts/nm. The "per nanometer" unit is omitted in the digital readout and is to be understood. Should the light from the emitting source not fill the solid acceptance angle of the instrument, it will be necessary to correct the readout by the ratio of the steradiancy subtended by the sample to that of the instrument. If the source is nearly a point source, or is far away from the instrument relative to its size, the spectrometer reading approaches irradiance. Irradiance is the amount of spectroradiometric power falling on the instrument aperture per unit area.

Weak luminescences will often require the use of the integrate mode in order to obtain increased sensitivity. The integrate mode takes advantage of the signal storage property of the silicon vidicon. The vidicon target is an array of photodiodes which are reverse-biased and are addressed by an electron beam. When light is impingent upon the target electron-hole pairs are created. The bias causes the electron to be conducted to ground and the hole to migrate to the side of the target addressed by the electron beam. This pattern remains on the target for a length of time long compared to the scanning period. This property provides the multiplex advantage of the vidicon: the ability to gather information at all wavelengths simultaneously. The integrate time is the time interval between passage of the electron beam past a diode on the target. It is the time available for the target to gather spectral information before it is detected and erased (discharged) by the electron beam. The time/scan control allows one to select integrate times of 50, 100, 200, 500 and 1000 ms. This number represents the length of time that scanning of the vidicon is held off plus the scan time. Thus, a given point on the vidicon is addressed by the electron beam at time intervals equal to the selected integrate time. The increase in responsivity of the system with integrate time is the result of the charge-storage property of the vidicon. The target acts very much like a photographic plate, gathering information continuously at all wavelengths being periodically "read off" by the electron beam. This multiplex advantage ensures that all spectral information is received and detected.

Luminescence decays may be studied with the Rapid Scan Spectrometer if their lifetimes fall into the useful response time of the instrument. The response time (the time required for a signal to fall to a given fraction of its original intensity) is dependent on the scan mode employed. The faster scan modes (10 and 20 ms) of course will have faster response times, allowing the electron beam to erase the target faster.

Going to longer integrate times allows one to trade off response time for sensitivity. The vidicon will allow one to follow decays with decay constants on the order of 30 milliseconds, but it should be emphasized that the exact response time depends on the initial intensity of the luminescence and on the scan mode chosen. For molecular luminescence, this clearly restricts the use of the RSS to measuring phosphorescence decay since fluourescence decays away on the order of nanoseconds. The response time is fastest for high intensities (below saturation, of course) and faster scan rates. One can choose an uncalibrated scan speed with an additional time base. Additionally, one can open the slits wide to maximize the initial intensity of the phosphorescence. It doesn't matter if resolution is lost as long as the entire spectrum decays with the same rate constant. Of course, this wouldn't be possible if one were studying decay kinetics as a function of wavelength, but even then some loss of resolution is not serious. Once the spectrum has been fully resolved, the adjustments just suggested can be made to study the kinetics of the decay.

Polarization studies can be made easily with the RSS by merely using polarizers in the excitation and in the observation paths. It should be pointed out, however, that the spectrometer, being a grating instrument, responds differentially to light with various orientations of plane-polarized light.

If sufficient excitation intensity is available, one could vary the wavelength of excitation and obtain the excitation spectra of fluorescence and phosphorescence with the unique advantage of observing the entire emission spectrum.

One additional property of the TEKTRONIX Rapid Scan Spectrometer is its sensitivity in the near infrared. The vidicon responds from the near UV (less than 250 nm) to the near IR (around 1100 nm). This response in the near IR is beyond most photocathodes and photographic plates. This opens up opportunities in research in molecular spectroscopy where emission takes place from low-lying electronic states of dyes, transition-metal ions, free radicals, plasmas, and other systems.

The use of a digital minicomputer with the RSS can greatly increase its utility by signal averaging, baseline correction, spectral correction, and data reduction. Computerization of the RSS will be covered in future Analytical Instruments application notes.

Experimental Results

A device was constructed (see Figure 3) in the applications laboratory which allowed excitation of a sample frozen to liquid nitrogen temperature. The excitation source is a 150W DC xenon arc which is filtered by means of Kasha[1] filter and is then focused on the sample. An electronic shutter is used to turn the excitation on and off. A line drawing appears in Figure 4. The quartz-iodine source was included for absorption work but was not used for the work reported here.

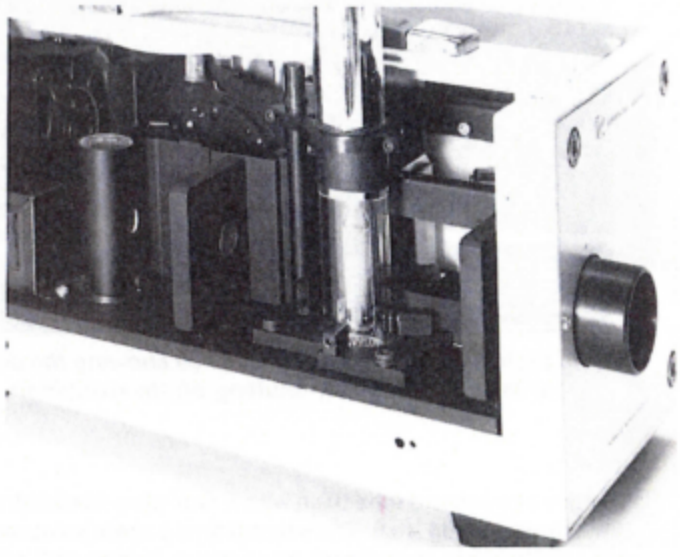


Fig. 3. Apparatus constructed for observing molecular luminescence at low temperature. A quartz optical dewar was employed with xenon excitation.

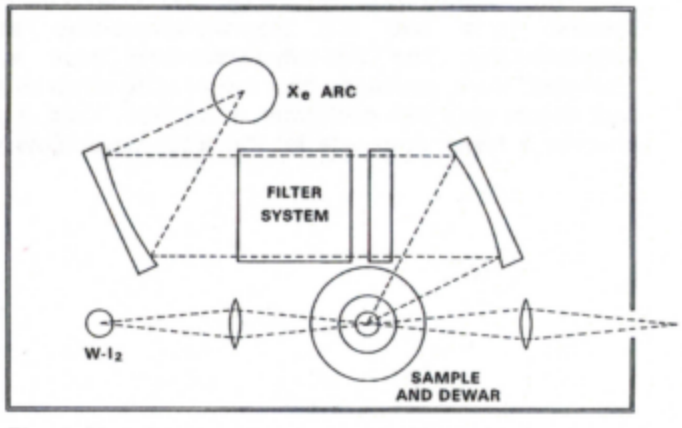


Fig. 4. Line drawing showing optical layout in luminescence apparatus.

Figure 5 shows the phosphorescence spectrum of diphenylamine. The wavelength of the intensified spot is read out digitally at the top of the screen. The CRT also reads the dispersion (nm/div), the time per scan (ms) and an indication of the vertical sensitivity (W). This vertical sensitivity reads in true optical power only when the "X" does not appear.

[1]M. Kasha, *J. Opt. Soc. Am.*, **38**, 929 (1948).

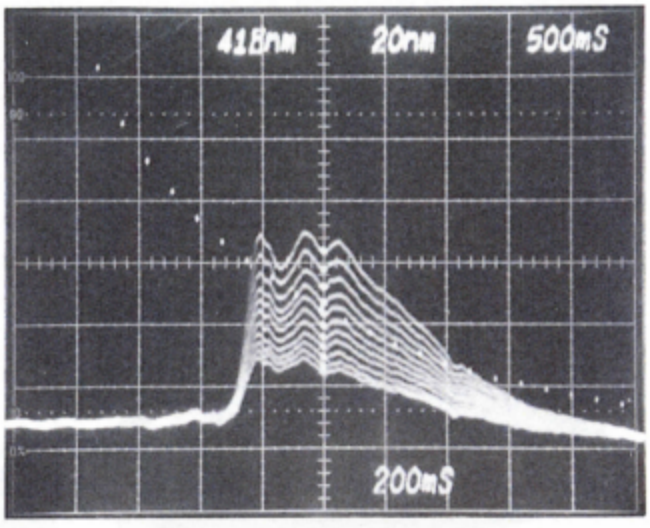


Fig. 5. Diphenylamine phosphorescence showing the decay of the spectrum after shutting off the excitation.

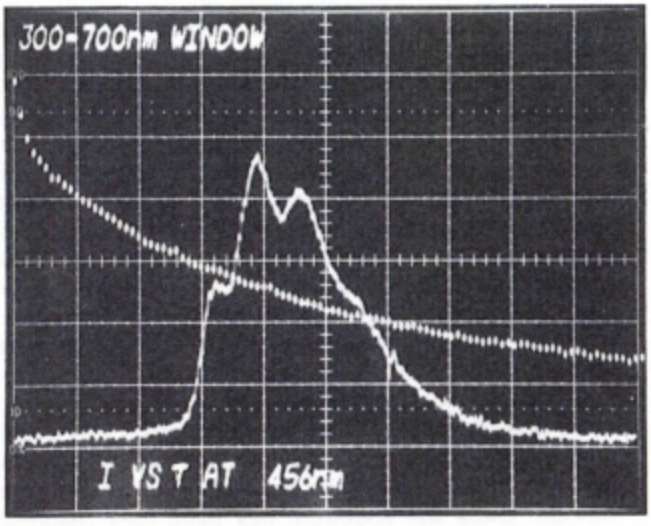


Fig. 6. Phosphorescence of biphenyl with the additional display of intensity versus time using the marker spot and an extra time base.

The use of a second time base with a four-plug-in mainframe is illustrated in Figure 6. The second time base is selected on the oscilloscope mainframe by pushing button "B" of the horizontal mode. The intensity of the trace is turned down until only the intensified spot (wavelength marker) remains on the screen. The time base can be triggered by the 7J20 through the mainframe, or externally with the same trigger used for the 7J20. By selecting the CHOP mode on the mainframe for the horizontal, one can display both the RSS spectral trace and the intensity-versus-time trace simultaneously. The intensity-versus-time trace is a "sampled" trace, appearing as a row of spots since such a spot occurs only with each trace of the RSS. Thus, if one chooses a faster scan rate for the RSS, more spots will appear. For very fast decays, the 4-ms uncalibrated scan rate would be the most useful providing both the maximum number of intensity samples per unit time and minimum response time for the system. The intensified spot can be moved to any part of the spectrum displayed to give intensity versus time information and the wavelength of the spot will appear digitally on the display screen of the oscilloscope. All of the quantities which appear digitally on the oscilloscope screen for the RSS and the second time base will appear when the CHOP mode is selected for the horizontal plug-in. For a convenient display, the VERTICAL TRACE SEPARATION control can be used to separate the decaying spectrum from the intensity versus time display.

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Triplet-Triplet Absorption

This note contains the results of a study of triplet-triplet absorption in organic molecules employing the TEKTRONIX J20/7J20 Rapid Scan Spectrometer (RSS).

Many measurements of triplet-triplet absorption (TTA) are carried out using steady-state excitation techniques. The sample is irradiated continuously while the absorption is scanned. The problem usually encountered is the generation of products which can give misleading transient absorptions. The correspondence of the decay lifetimes of TTA and phosphorescence are usually taken as strong evidence of their common triplet state origin.

The application of the TEKTRONIX J20/7J20 Rapid Scan Spectrometer to TTA offers a number of advantages to the measurement of TTA. Irradiation times are kept to a minimum, reducing the possibility of generating unwanted photoproducts. Decay data are easily obtainable to check the lifetime correspondences of TTA and phosphorescence. Additionally, the computer can be used to digest and treat all of the data. All spectral data can be held in the computer and only the desired results or spectral scans need necessarily by retrieved for permanent records.

Experimental

The experimental apparatus consists of a specially constructed sample box as illustrated in Figure 1. By two mirrors the light from a 150 W xenon DC arc (Osram XBO-150 W/1) is first collimated, then passed through a Kasha C' filter[1] after which it is then focused on the sample. The analyzing source of light consists of a small 25 W quartz-iodine bulb which is focused through the sample. An electronic shutter allows the ultraviolet irradiance to be turned on and off with about 2 ms resolution.

The sample consists of the organic molecules (usually about 10^{-4}M) in EPA (a mixture of ethyl ether, iso-pentane, and ethyl alcohol in a volume ratio of 5:5:2) in a suprasil quartz tube suspended in liquid nitrogen contained in a suprasil quartz optical dewar. The effective sample path length is approximately 1 cm. The rapid scanning spectrometer employed is the TEKTRONIX J20/7J20 used in a 7704A/P7001 Digital Processing Oscilloscope which is interfaced to a Digital Electronics Corp. PDP 11/05 computer. The EPA mixed solvent is manufactured by Matheson, Coleman and Bell.

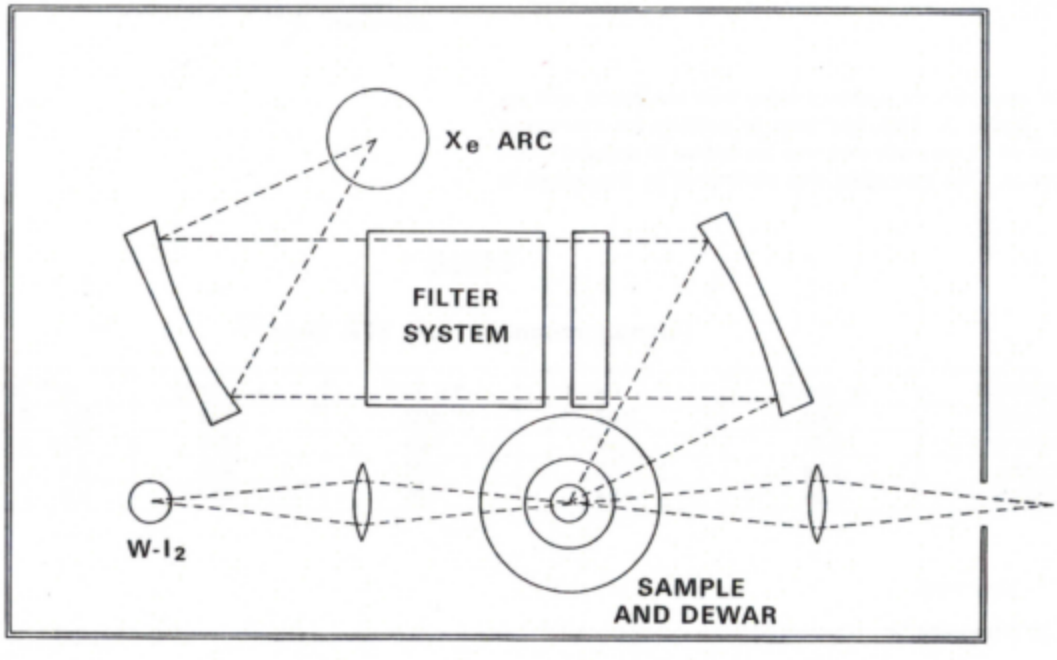

Figure 1.

References

1. M. Kasha, *J. Opt. Soc. Am.*, 38, 922 (1948).
2. B. R. Henry and M. Kasha, *Chem. Phy.*, 47, 3319 (1967).

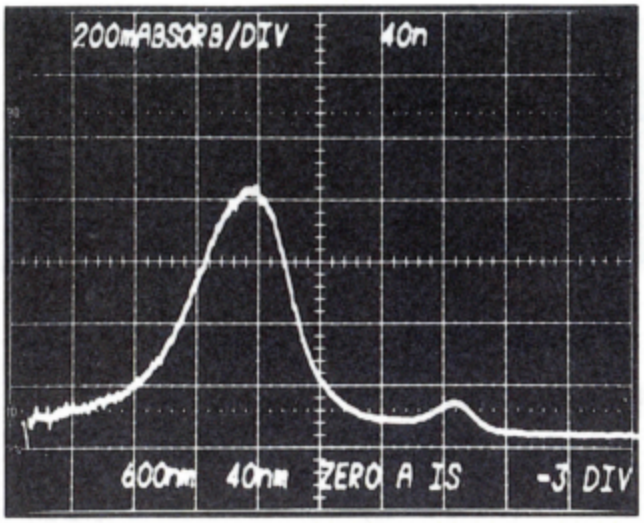

Figure 2.

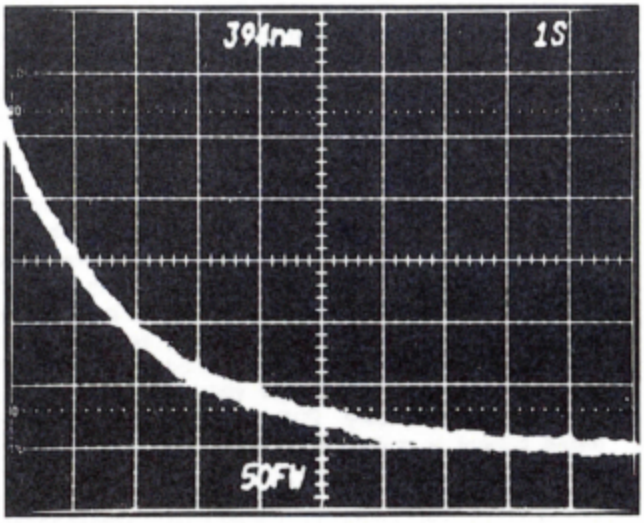

Figure 3.

Results

The TTA spectrum of diphenylamine was measured and appears in Figure 2. This spectrum is actually an average of 100 scans of 20 ms each and was measured in approximately two seconds. The averaging was performed by the computer using a routine built into the computer software. The decay data for the triplet-triplet absorption can be easily measured by employing an extra time base in conjunction with the spectrometer (cf Application Note No. 8). One can then obtain intensity versus time information for both the phosphorescence and TTA for immediate comparison. Figure 3 shows the decay of the diphenylamine phosphorescence at 394 nm with a one sec/div time scale. Figure 4 shows the absorbance decay of the diphenylamine TTA at 539 nm. The vertical scale is 0.1 absorbance units per division with a time scale of one sec/div. The results of all measurements appear in Table 1.

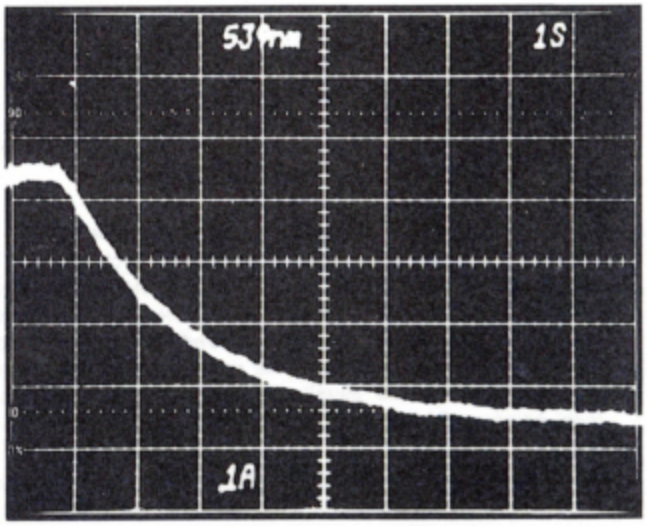

Figure 4.

Conclusion

The use of a multiplexing spectrometer coupled with a minicomputer makes triplet-triplet absorption a routine accomplishment minimizing the prospect of photoproduct generation. A projection to future work would be to include polarization measurements which could be performed on a similar time scale and calculations performed within the computer.

TABLE 1

Phosphorescence and TTA Data[1]

Compound	τ_P (sec.)	τ_{T-T} (sec.)	λ_P (nm)	λ_{T-T} (nm)	τ_P[2] (sec.)	τ_{T-T}[2] (sec.)
Diphenylamine	2.02	2.02	400	539	2.1 ± 0.2	1.9 ± 0.2
Triphenylamine	0.71	0.76	400	505	0.74 ± 0.05	0.9 ± 0.2
Phenoxazine	3.28	3.03	485	446	2.2	2.7 ± 0.2
Phenanthrene	4.08	4.24	485	467	3.3	3.9 ± 0.8

Notes: 1. This work

2. Reference 2