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TITLE: LASER-BASED INSTRUMENTATION FOR DETECTION OF CHEMICAL-WARFARE AGENTS

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Laser-Based Instrumentation for Detection of Chemical-Warfare Agents*

by

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ABSTRACT

Several laser-based techniques are being developed for remote, point, and surface contamination detection of chemical warfare agents. These techniques include optoacoustic spectroscopy, laser-induced breakdown spectroscopy, and synchronous detection of laser-induced fluorescence. Detection limits in the part-per-million to part-per-billion regime have been demonstrated.

*Work performed under the auspices of the US DOE

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I. Introduction

In the modern, integrated battlefield, operating areas, equipment, and personnel are subject to contamination by chemical warfare agents. This scenario requires that rapid agent detection techniques be developed for contamination avoidance as well as certification of hardware decontamination. To address these issues, scientists at the Los Alamos National Laboratory have been developing laser-based methods for the detection of chemical warfare agents. These optical techniques afford extremely sensitive remote, point, and surface contamination detection capabilities. Furthermore, detection can be accomplished in real-time.

Among the laser-based detection approaches being developed at Los Alamos are optoacoustic spectroscopy, laser-induced breakdown spectroscopy (LIBS), and synchronous detection of laser-induced fluorescence (SDLIF). In laboratory tests optoacoustic spectroscopy has been used to detect agent GB at the 10 ppb level. Laser-induced breakdown spectroscopy has been used to monitor species concentrations in the part-per-million to part-per-billion regime. Development of the SDLIF technique was only recently begun, but it promises to be a sensitive scheme for both remote and surface detection.

II. Optoacoustic Spectroscopy

The physical basis for optoacoustic detection is that following vibrational excitation of a molecular species, the vibrational energy is ultimately degraded to heat, producing a pressure wave in the surrounding gas. If the excitation source (typically an infrared laser) is modulated, the acoustic signal occurs at the modulation frequency and may be detected with a microphone. Furthermore, the sound

intensity is a direct function of the absorbed energy. Thus, by increasing the power of the laser source the acoustic signal may be enhanced. This feature of optoacoustic detection, coupled with the frequency tunability of many laser sources, provides the capability to det ' specific trace components dispersed in the atmosphere.

We have employed the optoacoustic technique to detect agent GB at ppb concentrations in air. The apparatus employed is depicted schematically in Fig. 1 and consists of a line-tunable, cw CO_2 laser, a sample cell equipped with a microphone, a chopper-wheel to modulate the CO_2 laser beam intensity, and a lock-in amplifier for signal processing. Several infrared absorption features of agent GB occur in the 9-11 μm region as shown in the upper portion of Fig. 2. This spectral range is conveniently covered by laser lines derived from the CO_2 laser, as indicated in the lower section of Fig. 2.

A dilution apparatus was used to prepare samples of GB in air. Initially, N_2 was passed over a porous material impregnated with GB. The N_2 flow was then further diluted by a measured flow of dry air. In this manner air samples containing ppb concentrations of GB could be prepared in order to determine the efficacy of agent detection via optoacoustic spectroscopy. The signal level obtained from an air sample containing 10 ppb of GB is shown in Fig. 3. Since the background signal (also presented in Fig. 3) is much smaller in magnitude, it is clear that optoacoustic detection provides an extremely sensitive means for monitoring the presence of chemical agents.

The dependence of the optoacoustic signal from agent GB has also been determined as a function of CO_2 laser wavelength. As indicated previously, the optoacoustic signal level is proportional to the absorbed energy. Hence, the signal should mimic the infrared spectrum of the material under study, allowing positive identification of a material if a sufficient spectral region can be explored. As may be seen in Fig. 4, over the limited spectral region investigated, the opto-

acoustic spectrum of GB does indeed coincide with the low resolution infrared spectrum.

III. Laser-Induced Breakdown Spectroscopy

Laser-Induced breakdown spectroscopy has proven to be an extremely sensitive method for monitoring various airborne contaminants, both in molecular form and as aerosols. The technique is based on generating a plasma with the focused output of a high-intensity, pulsed laser. The molecules and particulates within the plasma volume are typically reduced to elemental form, producing electronically excited ionic or neutral atomic species. Emission from these excited atoms may be detected, allowing identification of particular elements from their characteristic spectral signatures. The application of LIBS to the detection of chemical agents is predicated on monitoring emission from the unique combination of elements which are typically present in the agents. In the case of nerve agents these elements are phosphorus and fluorine (except agent GA which does not contain fluorine), while mustards generally incorporate sulfur and chlorine.

The apparatus used to determine the atomic spectral lines which provide the optimum detection sensitivity via LIBS is shown in Fig. 5. The focused output of a Nd:YAG laser (10 ns pulse length, ~ 100 mJ/pulse) produces the plasma. A monochromator equipped with a photomultiplier is used to monitor individual spectral lines from the plasma emission. A signal averaging system is employed to enhance the signal-to-noise (S/N) ratio. An essential feature of the detection electronics is that a delay time may be introduced between plasma initiation and recording of the emission. It has been found that in the early stages of the plasma a broad continuum emission underlies spectral lines from singly ionized atoms. This behavior is shown in Fig. 6 for the phosphorus lines originating from the agent simulant diisopropyl methyl phosphonate (DIMP) dispersed in air. As the plasma evolves in time, the intensities of both the continuum and singly ionized atomic emission decay, while emission due to neutral atoms becomes more prevalent. In Fig. 7 this

behavior is shown for DIMP. Consequently, the S/N ratio is optimized in the LIBS technique by introducing a delay time between plasma onset and monitoring of neutral atomic emission. This approach is referred to as time-resolved laser-induced breakdown spectroscopy (TRELIBS). The effect of delay time on the S/N ratio for fluorine and chlorine emission lines is presented in Fig. 8.

The TRELIBS detection limit for phosphorus under laboratory conditions has been established as 1 ppm. If this value is specified as a concentration in mg/m^3 and compared to the median incapacitating doses (MID) of the agents containing phosphorus,[1] it is found that detection limit for the atoms is a factor of 5-50 lower than the MID.

IV. Synchronous Detection of Laser-Induced Fluorescence

In the application of the laser-induced fluorescence (LIF) technique to the detection of toxic chemicals in the environment, one finds that there are two interference problems that limit its usefulness. The first problem is interference due to background fluorescence from large concentrations of chemicals (either natural or man-made) which are an accepted part of the environment. The second problem is interference caused by the overlap of the fluorescence spectra of two or more of the chemical agents to be detected. Examples of the former problem are: dyes and paints; smoke and dust particles; natural pigments such as the chlorophyll in plants; and insecticides. These interference problems can be minimized by using a variation of the conventional LIF technique called synchronous detection of laser-induced fluorescence (SDLIF).

The essence of this process can be shown by reference to Fig. 9a, which is the conventional fluorescence excitation and emission spectrum of perylene in ethanol.[2] Note that the width of the emission spectrum that one would see in normal laser-induced fluorescence is about 50 nm, while the width of the synchronous spectrum (Fig. 9b) is 8 nm. The reduction in the width of the detected fluorescence spectrum is accomplished by scanning a narrow-band excitation source synchronously with a

narrow-band detector (a spectrometer with a photomultiplier tube at the output slit) at a fixed wavelength separation ($\Delta\lambda$). In the case of Fig. 9, $\Delta\lambda$ = 3 nm. What one measures then is the overlap integral of the excitation and emission spectrum, where $\Delta\lambda$ is a wavelength shift that optimizes the overlap and hence the signal intensity and spectral bandwidth.

We are developing a system that will improve this technique by substituting a tunable laser for the usual xenon arc lamp source. This will greatly increase the detection sensitivity of the technique (by greater than three orders-of-magnitude) and allow for a remote-sensing capability due to the collimated nature of the coherent laser source.

Figure 10 shows a block diagram of the simple experimental setup required to perform synchronous detection of LIF. A wavelength tunable-dye laser excites the sample in the cell and the fluorescence is viewed in the transverse direction by a spectrometer that is being scanned at the same rate as the laser, but is at a fixed wavelength separation, $\lambda_L - \lambda_S = \Delta\lambda$, where λ_L and λ_S are the laser and spectrometer wavelengths, respectively.

The choice of $\Delta\lambda$ is determined by several factors. The smaller the $\Delta\lambda$, the more one must contend with the effects of scattered laser light. With this in mind, $\Delta\lambda$ should be chosen to optimize the spectral intensity and bandwidth of each molecular component in the mixture. This optimum $\Delta\lambda$ is heavily dependent on the relative position of the excitation and emission spectra of each component. This can be seen more clearly by referring to Fig. 11 which shows (schematically) three general classes of fluorescing molecules divided according to the degree of overlap of the excitation and emission spectra. Clearly, $\Delta\lambda$ has a strong influence on the width of the synchronous spectrum. One would expect most molecules of interest to fall into category (b) where there is some overlap of the bands. In this case, if $\delta\lambda_S$ (the separation between bands) is large enough to avoid scattered light problems, the optimum condition is $\Delta\lambda = \delta\lambda_S$. For most molecules of interest here, this

is approximately 3 nm.

For simplicity, we have chosen tetracene for our first SDLIF studies. This is because the emission-absorption band overlap occurs in the middle of the Coumarin 480 (C480) dye laser gain characteristic and dye changes in mid-spectrum are not necessary.

As a point of comparison, we first took the normal LIF spectrum of tetracene in benzene, pumping the molecule at 470 nm with a fixed C480 laser output. This result is shown in Fig. 12, where the large spike at 470 nm is the pump laser light scattered into the SPEX spectrometer. Note that the tetracene spectrum is more than 90-nm wide.

On the other hand, the SDLIF spectrum of tetracene in benezene is shown in Fig. 13. In this case, both the dye laser and the spectrometer are scanned at the same rate and $\Delta\lambda$ = 5 nm. The result is that the tetracene fluorescence occupies no more than 7 nm (FWHM) of the spectrum, leaving room on either side for the detection of other fluorescing molecules whose LIF spectra overlap the tetracene spectrum, but whose SDLIF spectra are completely resolvable. Note that a 2×10^{-5} M solution of tetracene in benzene is equivalent to two parts-per-million in the condensed phase.

We are currently in the process of extending the SDLIF technique to the detection of chemical agents

References

1. U. S. Army FM 3-9, "Military Chemistry and Compounds," October 1975; Table 2-1.
2. T. Vo-Dinh, "Synchronous Excitation Spectroscopy," in Modern Fluorescence Spectroscopy, Vol. 4, E. L. Wehry, Ed., Plenum Press, New York, NY, 1981 (in press).

OPTO-ACOUSTIC DETECTION

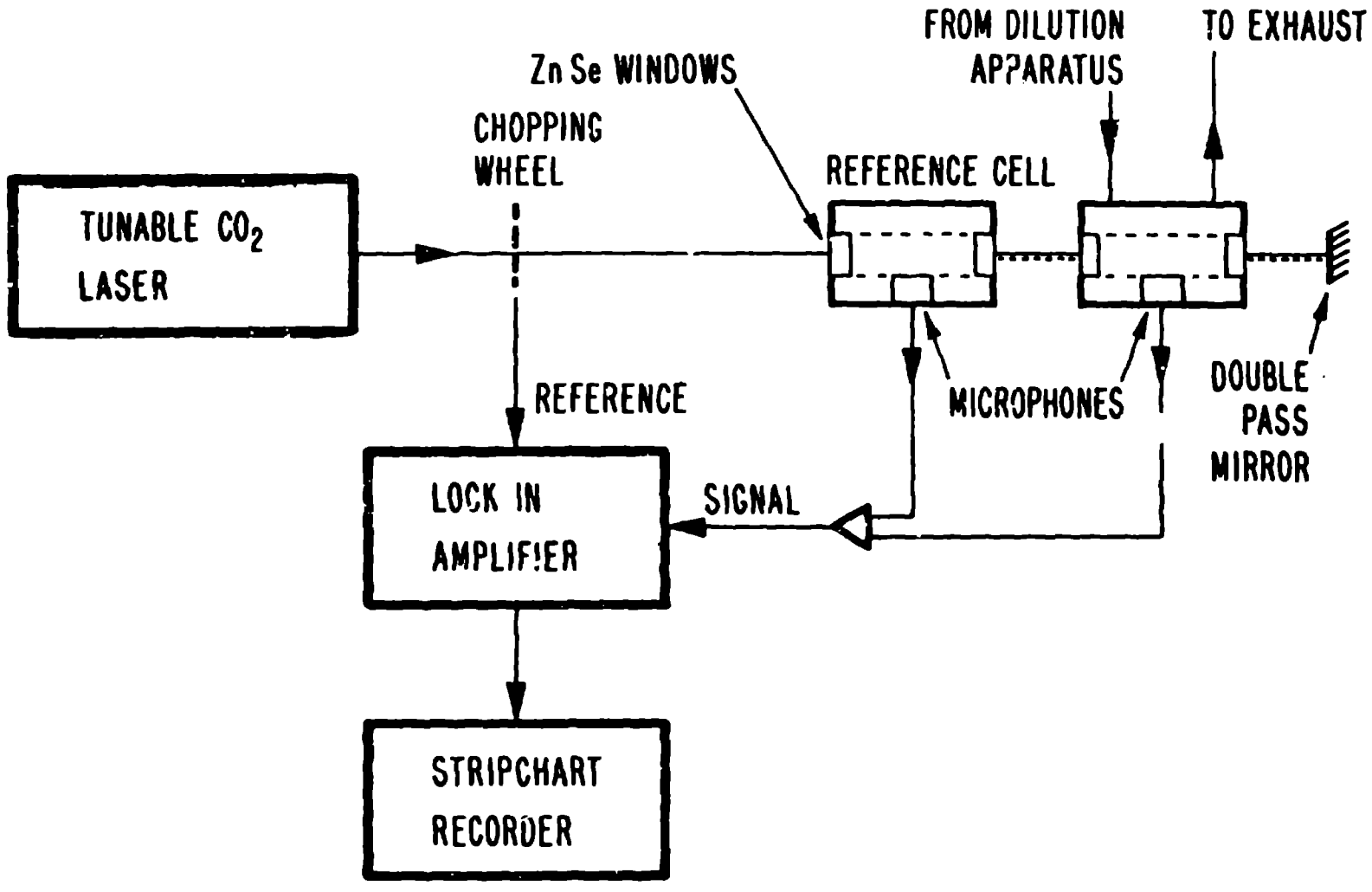

FIGURE 1. OPTOACOUSTIC DETECTION APPARATUS. The modulated output from a line-tunable, cw CO_2 laser generates an acoustic signal in a cell containing the sample of interest. A microphone integral to the cell senses the acoustic wave. A lock-in amplifier is used to detect the in-phase signal

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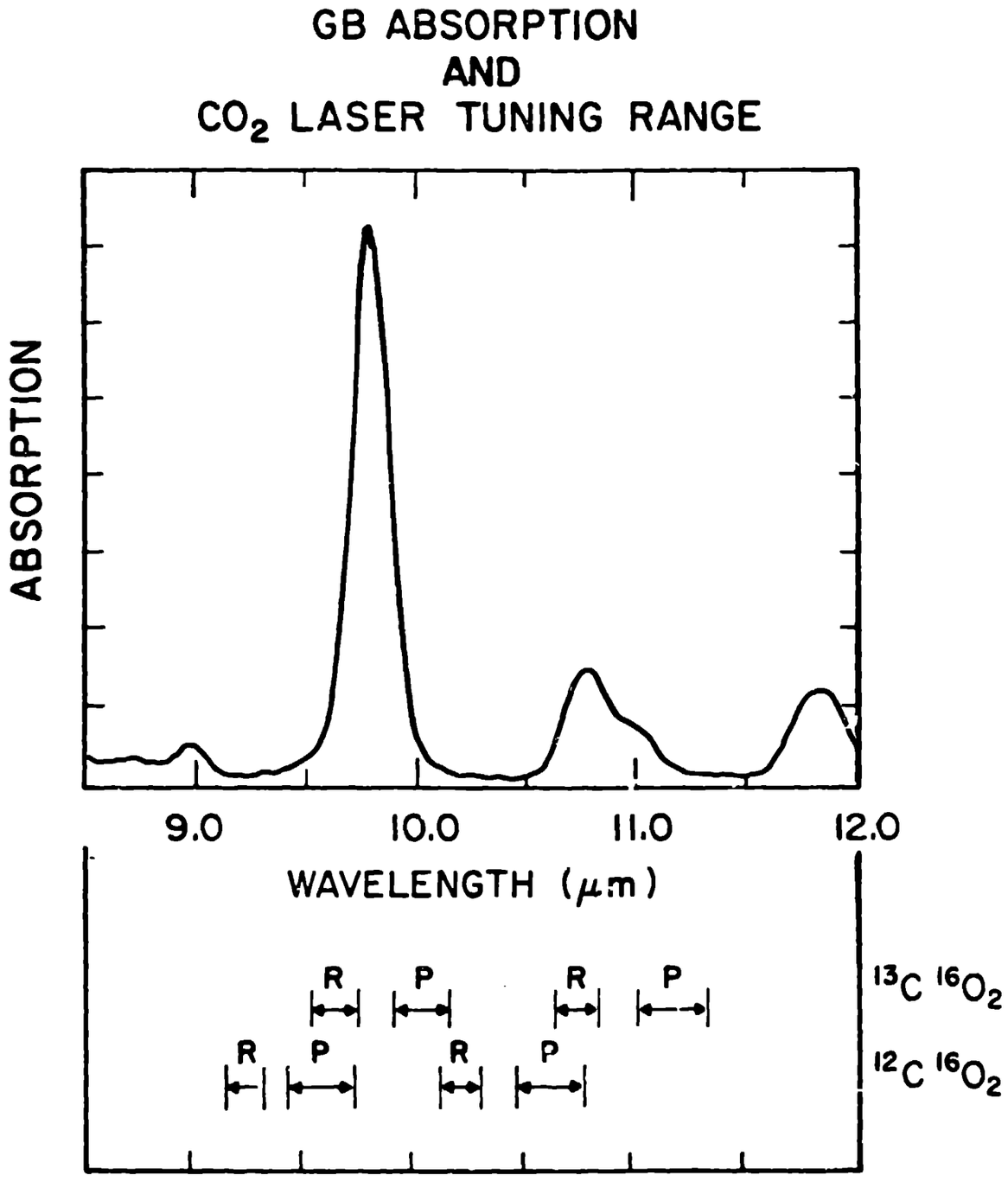

FIGURE 2. INFRARED ABSORPTION SPECTRUM OF AGENT GB. The upper spectrum shows several of the infrared absorption features of agent GB. Below is the spectral region accessible with a CO_2 laser.

OPTO-ACOUSTIC DETECTION

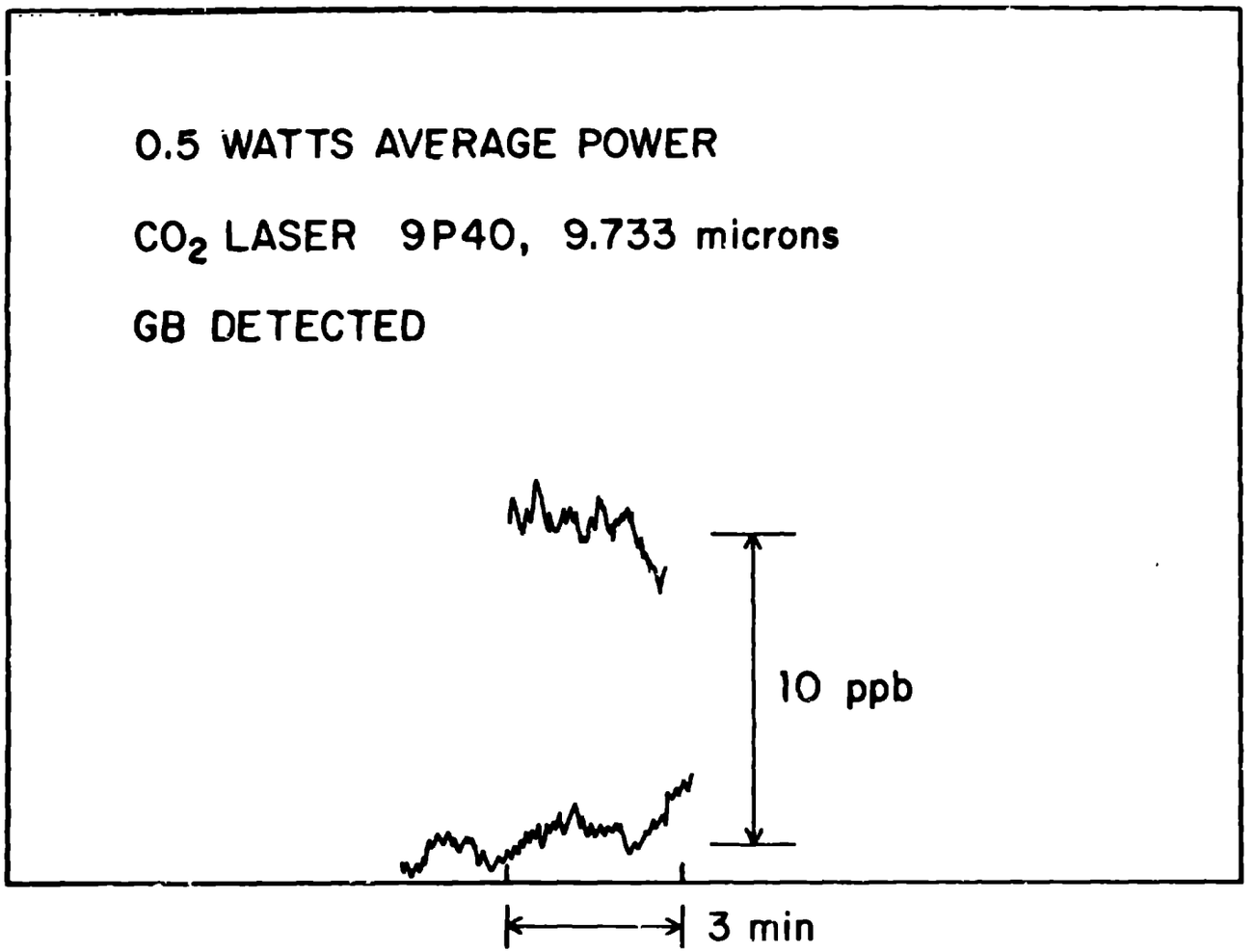

FIGURE 3. OPTOACOUSTIC DETECTION OF AGENT GB. The acoustic signal obtained from 10 ppb of agent GB in air.

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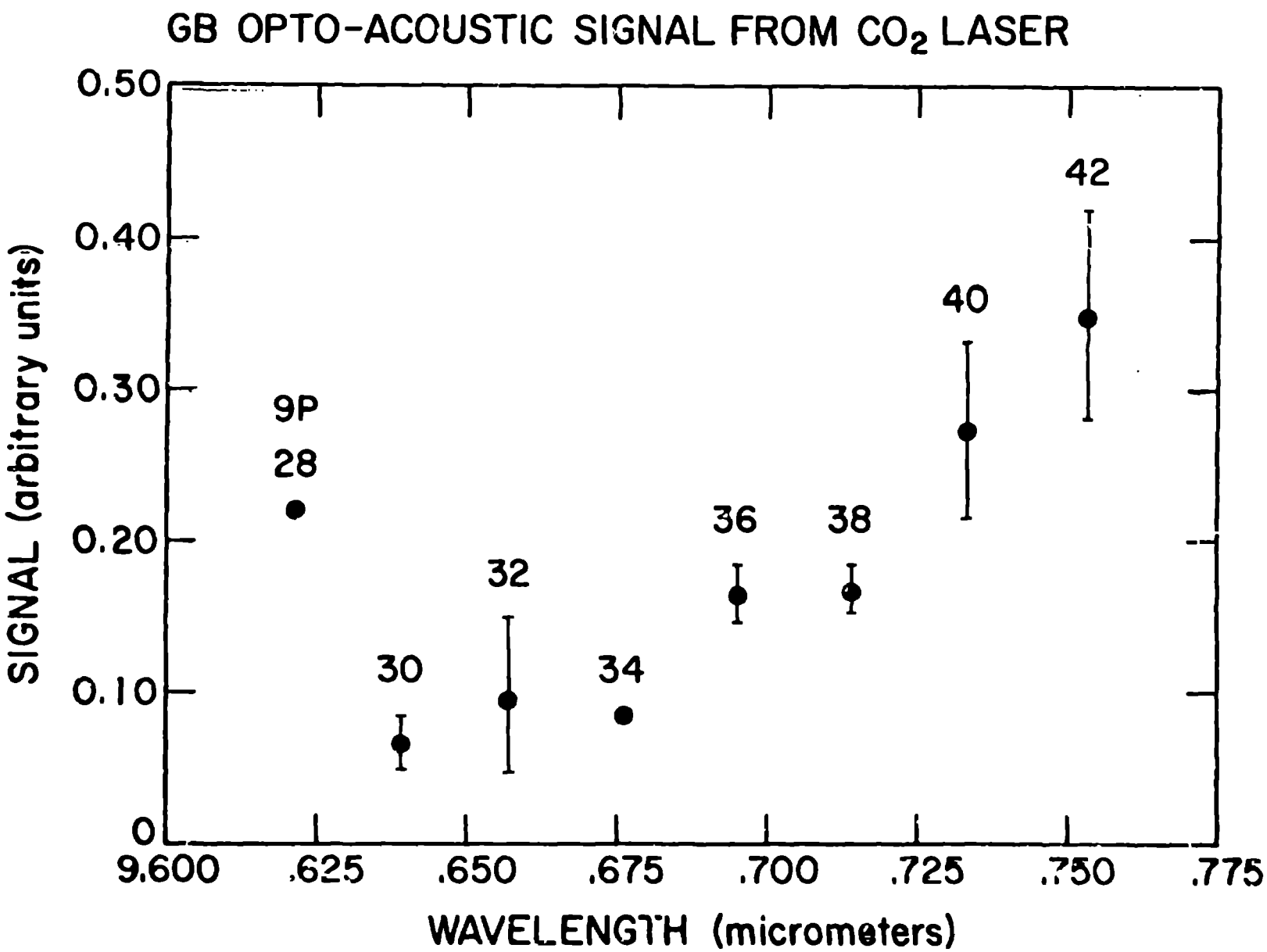

FIGURE 4. WAVELENGTH DEPENDENCE OF THE OPTOACOUSTIC SIGNAL FROM AGENT GB. The optoacoustic signals obtained from agent GB for several CO_2 lines. The optoacoustic spectrum mimics the low resolution infrared spectrum.

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TRELIBS APPARATUS

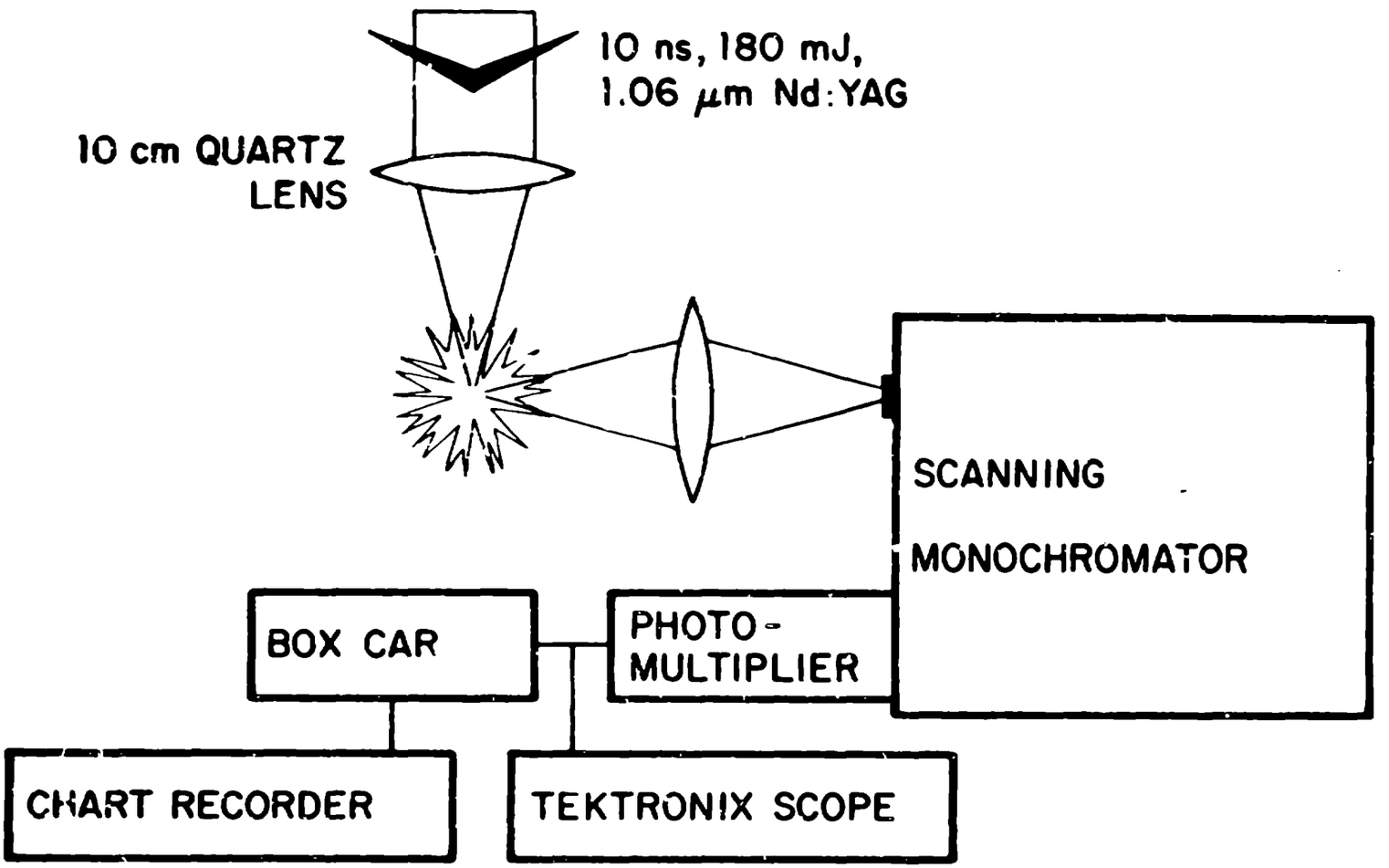

FIGURE 5. APPARATUS FOR PERFORMING TIME-RESOLVED LASER-INDUCED BREAKDOWN SPECTROSCOPY. A pulsed Nd:YAG laser produces a plasma. Emission from the plasma is spectrally resolved with a scanning monochromator.

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DETECTION OF PHOSPHOROUS IN A LASER INDUCED BREAKDOWN SPECTRUM OF DIMP

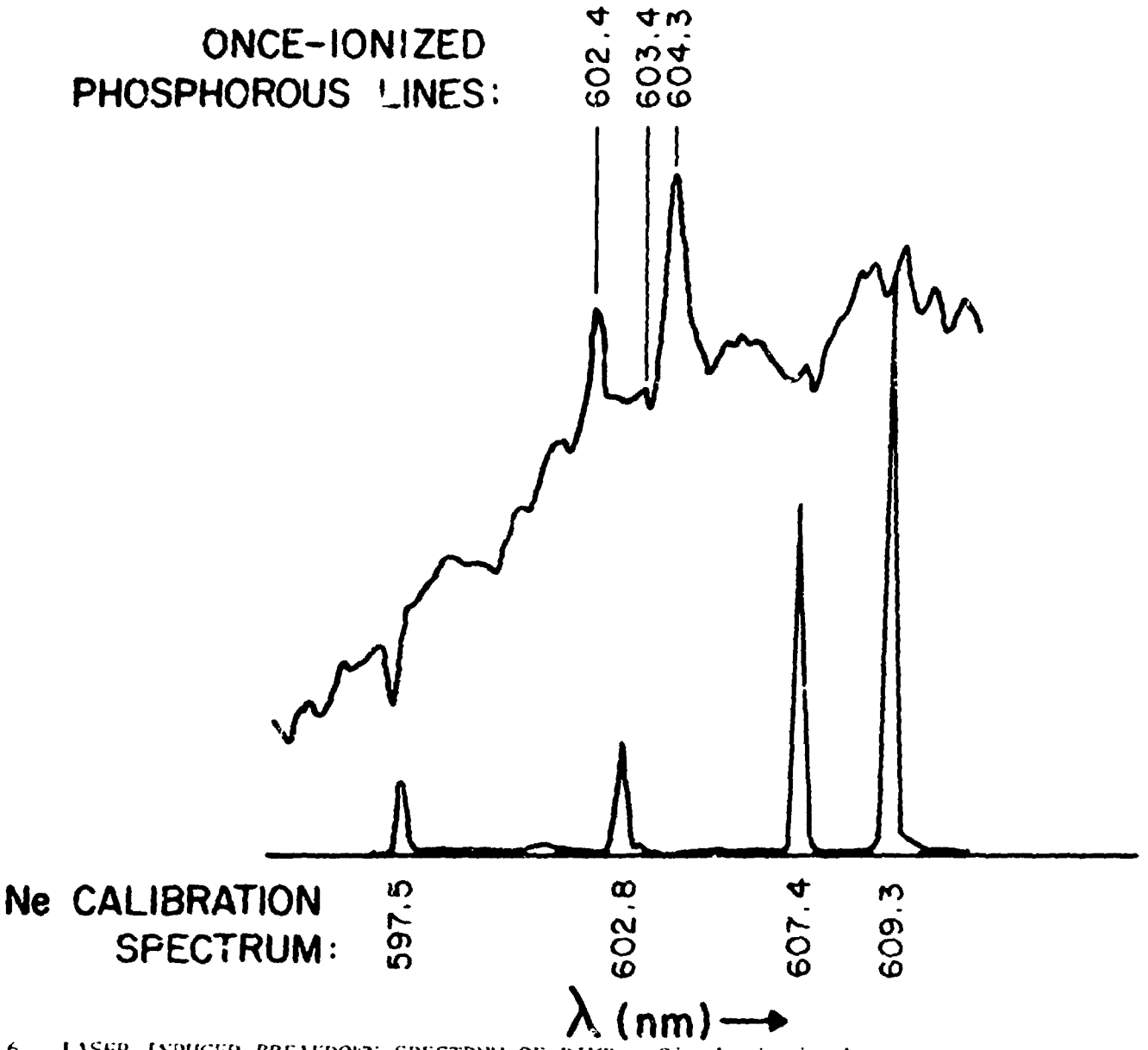

FIGURE 6. LASER-INDUCED BREAKDOWN SPECTRUM OF DIMP. Singly-ionized phosphorus lines lying on top of a background continuum emission are observed.

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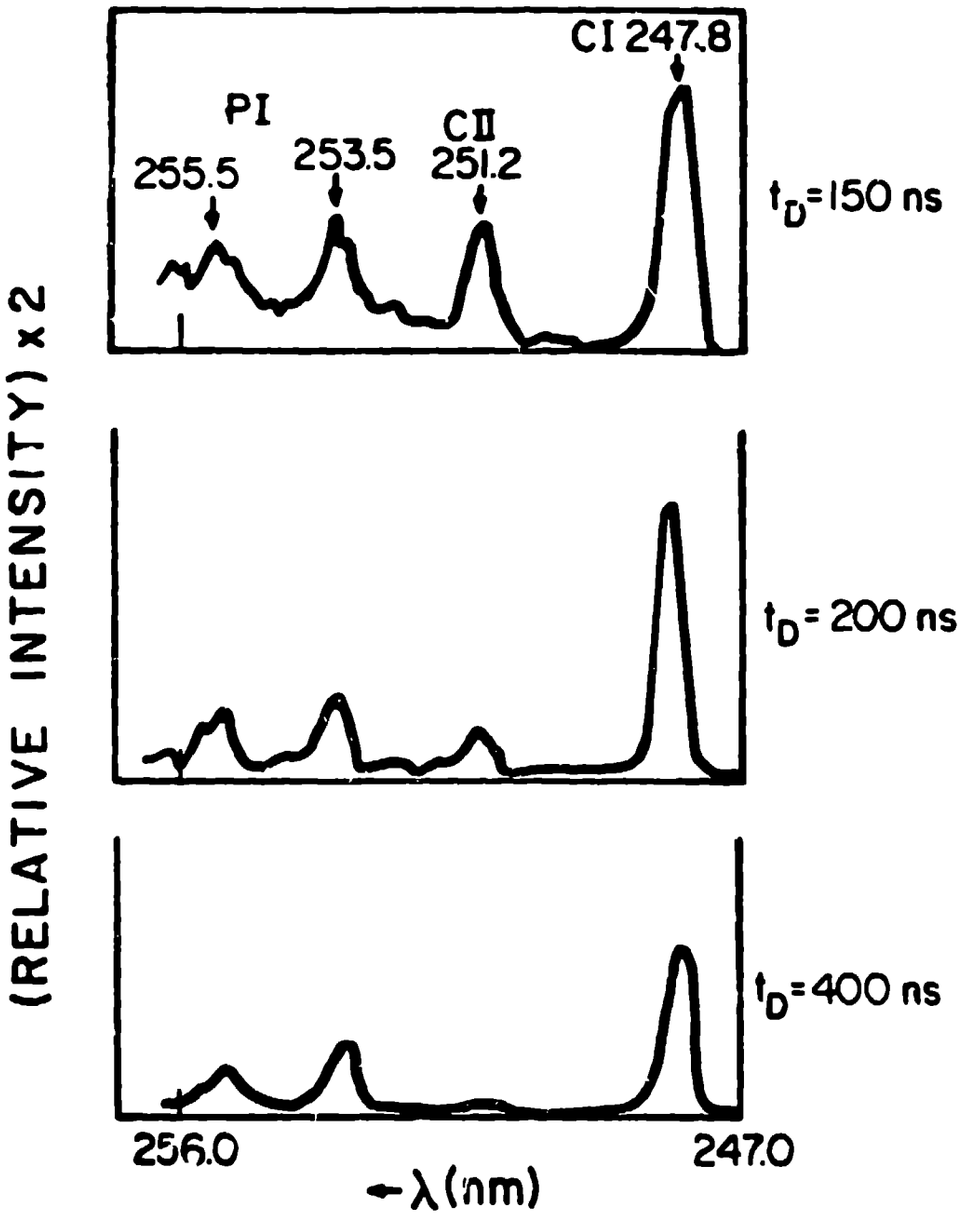

EMERGENCE OF PI LINES IN A ND:YAG LASER INDUCED PLASMA

FIGURE 7. EFFECT OF DELAY TIME ON THE LASER-INDUCED BREAKDOWN SPECTRUM OF DIMP. As the delay time between plasma onset and detection of emission is increased, neutral atomic lines become more pronounced while singly-ionized lines decrease in intensity.

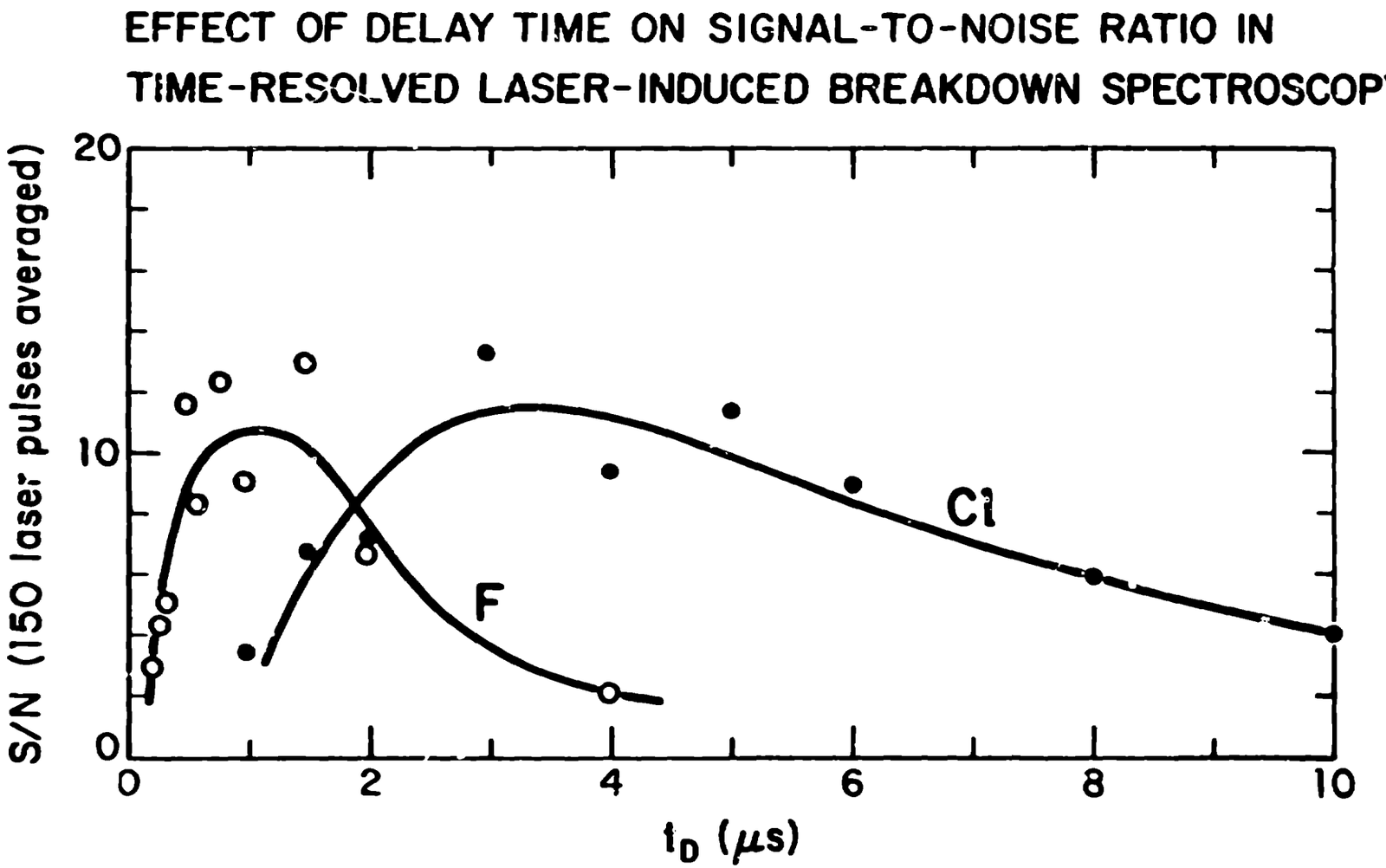

FIGURE 8. EFFECT OF DELAY TIME ON THE SIGNAL-TO-NOISE RATIO IN LASER-INDUCED BREAKDOWN SPECTROSCOPY. Shown are the signal-to-noise ratios for chlorine and fluorine atomic emissions as a function of time following plasma initiation.

AP-I-VG-8275

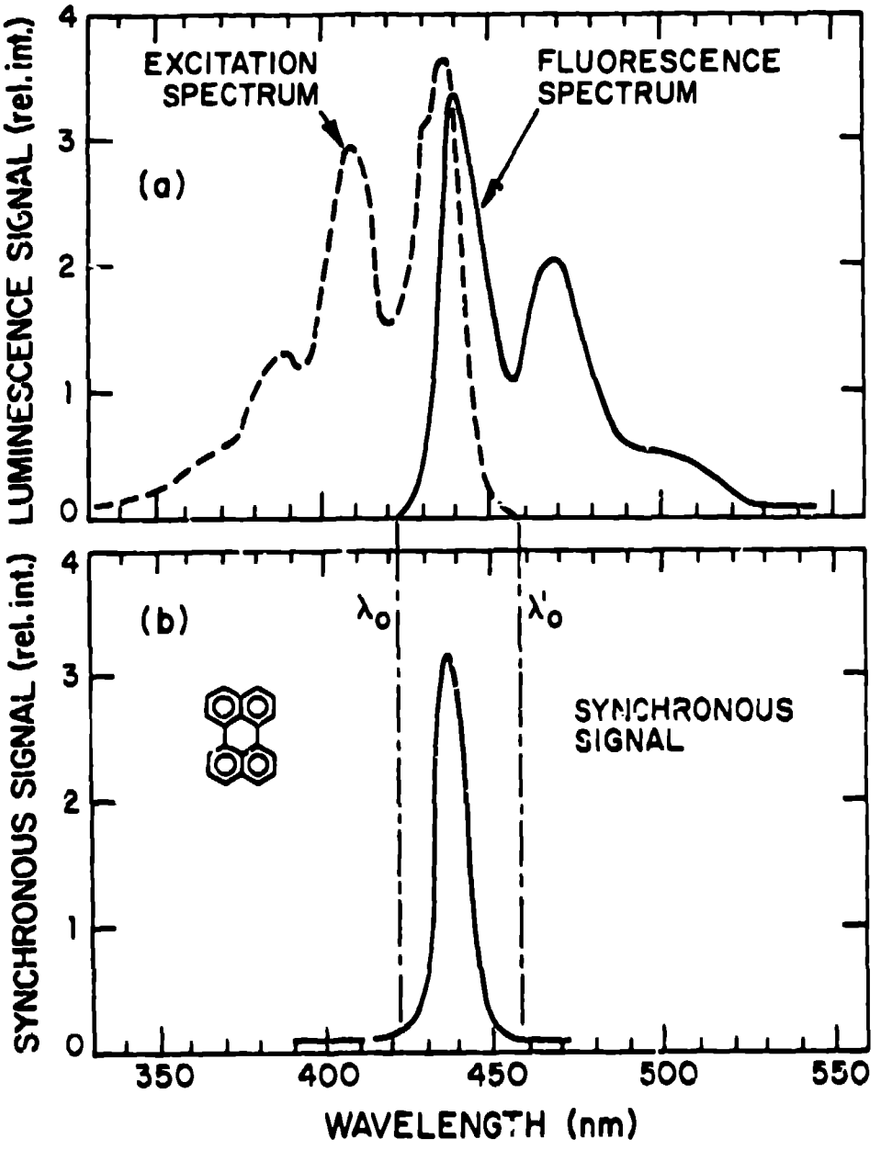

FIGURE 9. COMPARISON OF CONVENTIONAL AND SYNCHRONOUS DETECTION OF FLUORESCENCE. a) Excitation and fluorescence emission spectra of perylene. b) Synchronous detection of fluorescence from perylene showing dramatic narrowing of signal width in comparison to conventional fluorescence spectrum.

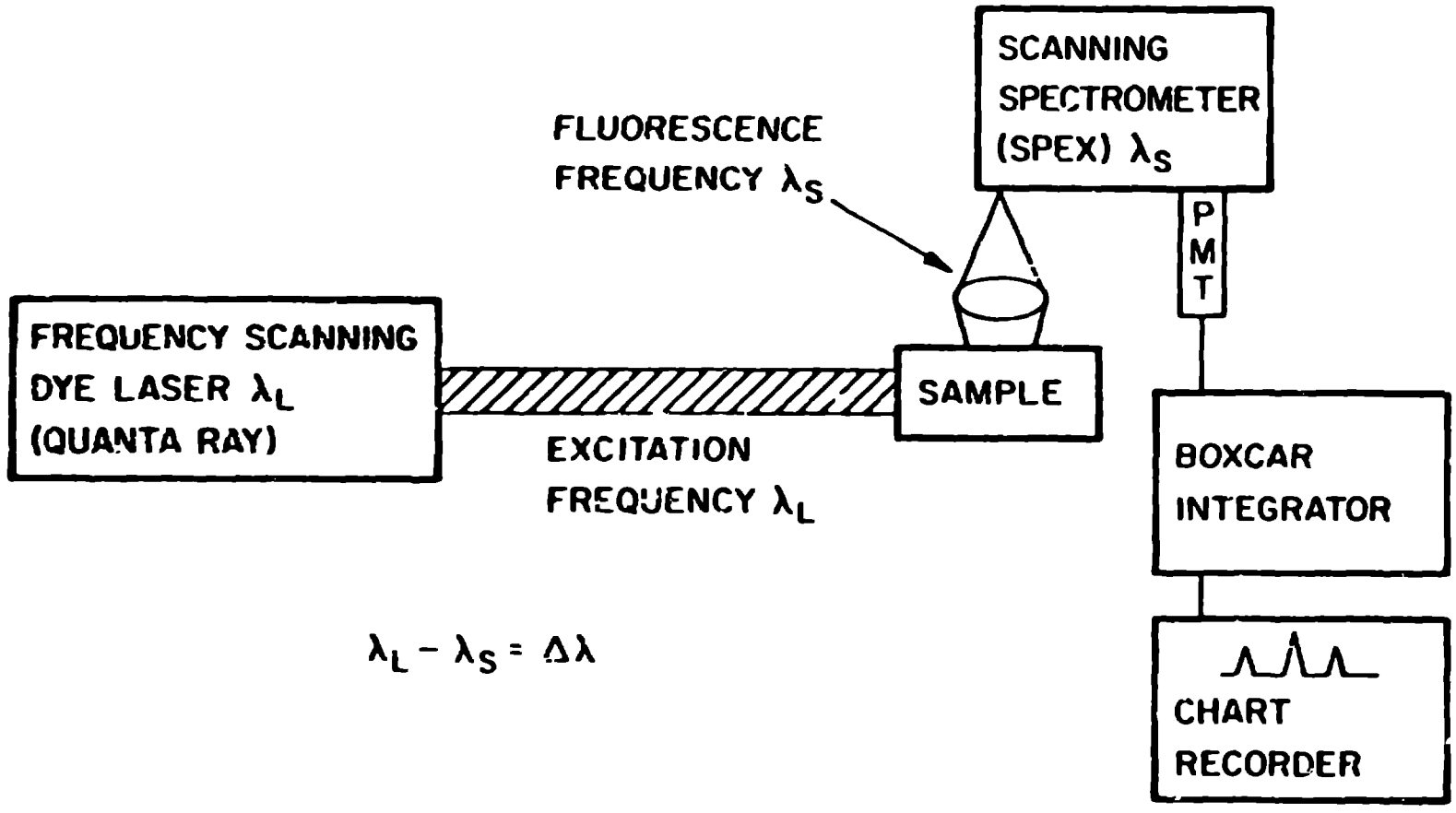

FIGURE 10. APPARATUS FOR SYNCHRONOUS DETECTION OF LASER-INDUCED FLUORESCENCE. A tunable laser and spectrometer are scanned synchronously at a fixed wavelength separtion. The laser produces the fluorescence in the sample, while the spectrometer detects this fluorescence.

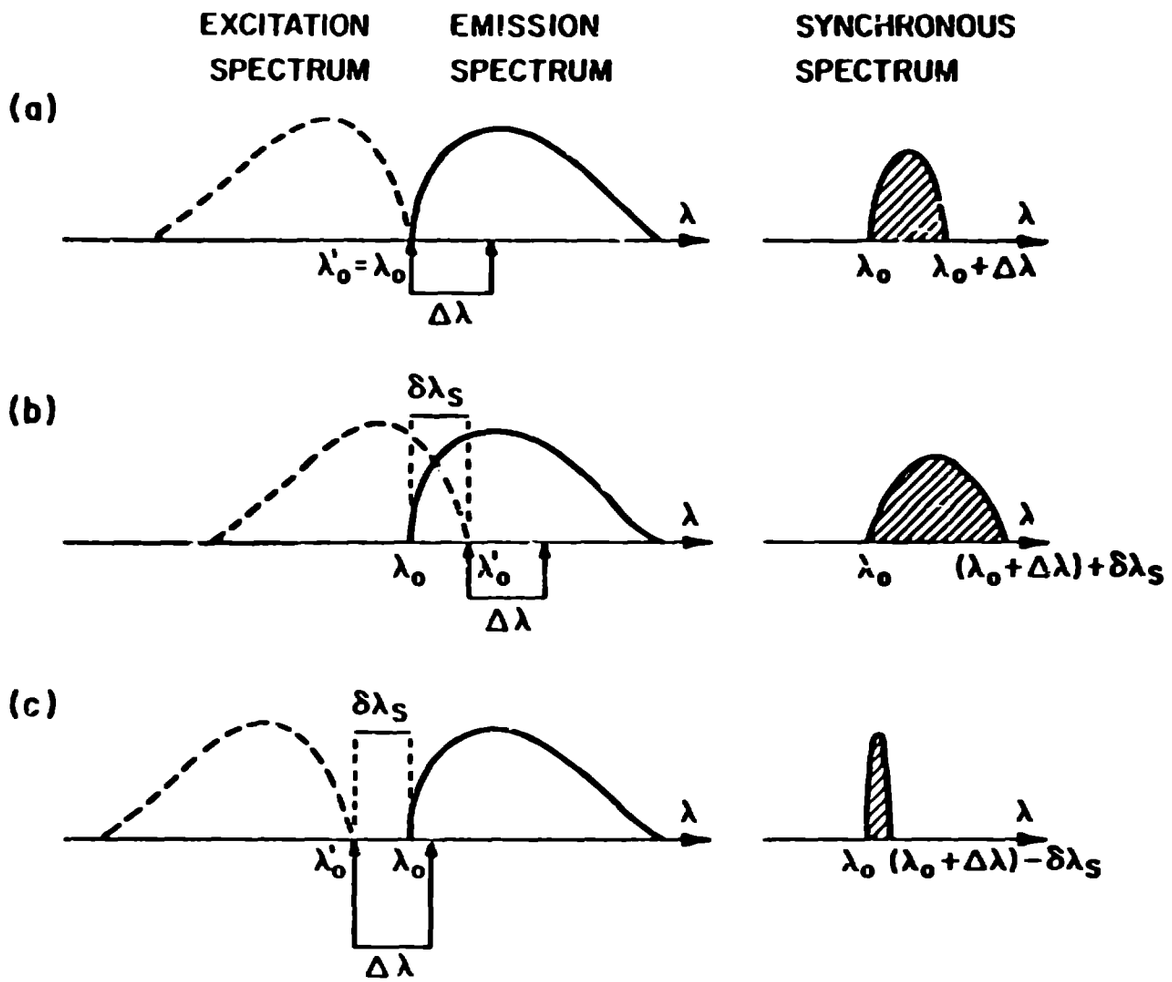

FIGURE 11. SYNCHRONOUS SPECTRUM OBTAINED FOR MOLECULES HAVING DIFFERENT RELATIONSHIPS BETWEEN EXCITATION AND EMISSION SPECTRA.

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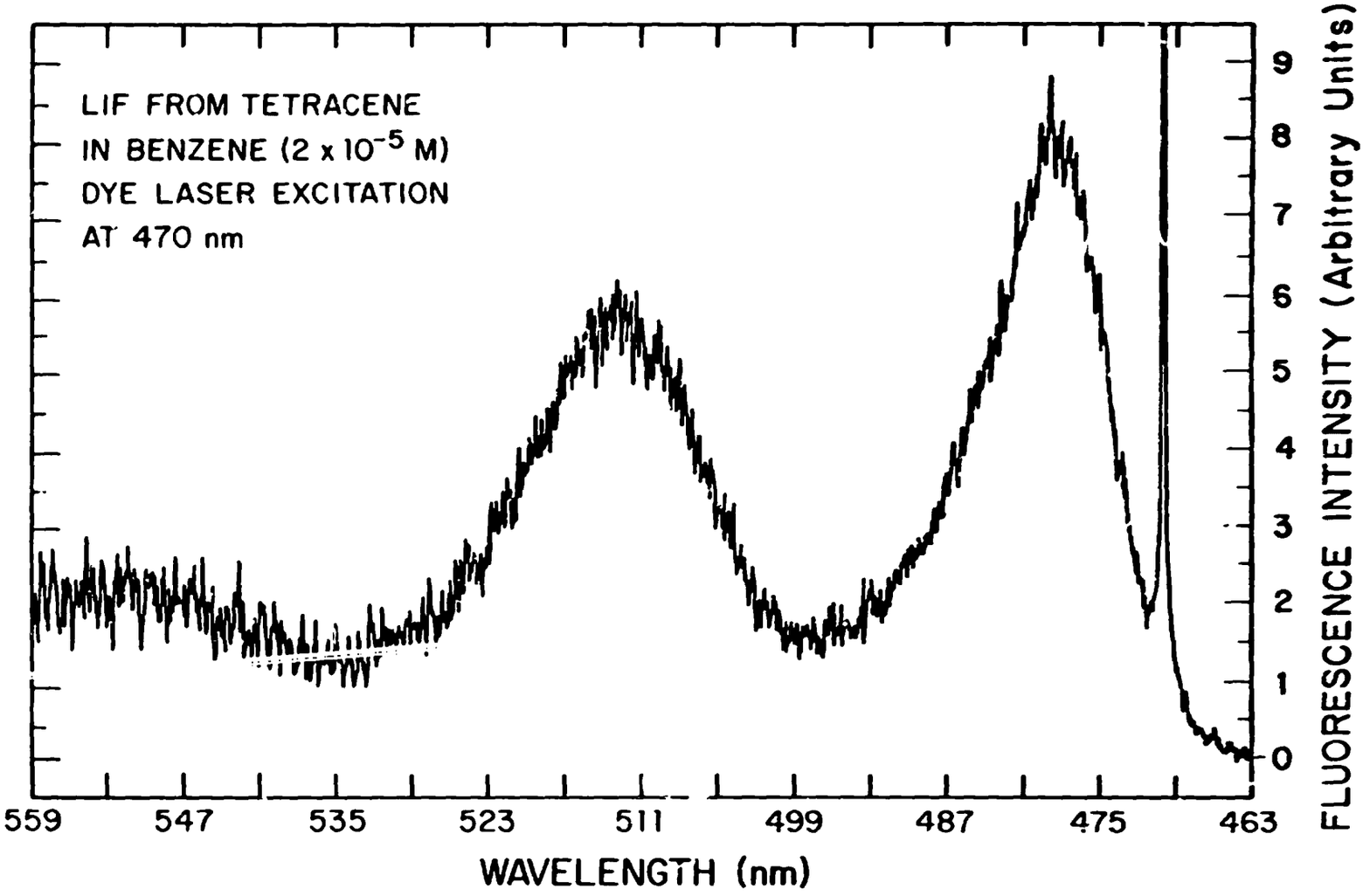

FIGURE 12. LASER-INDUCED FLUORESCENCE EMISSION SPECTRUM OF TETRACENE.

AP-1-VG-8274

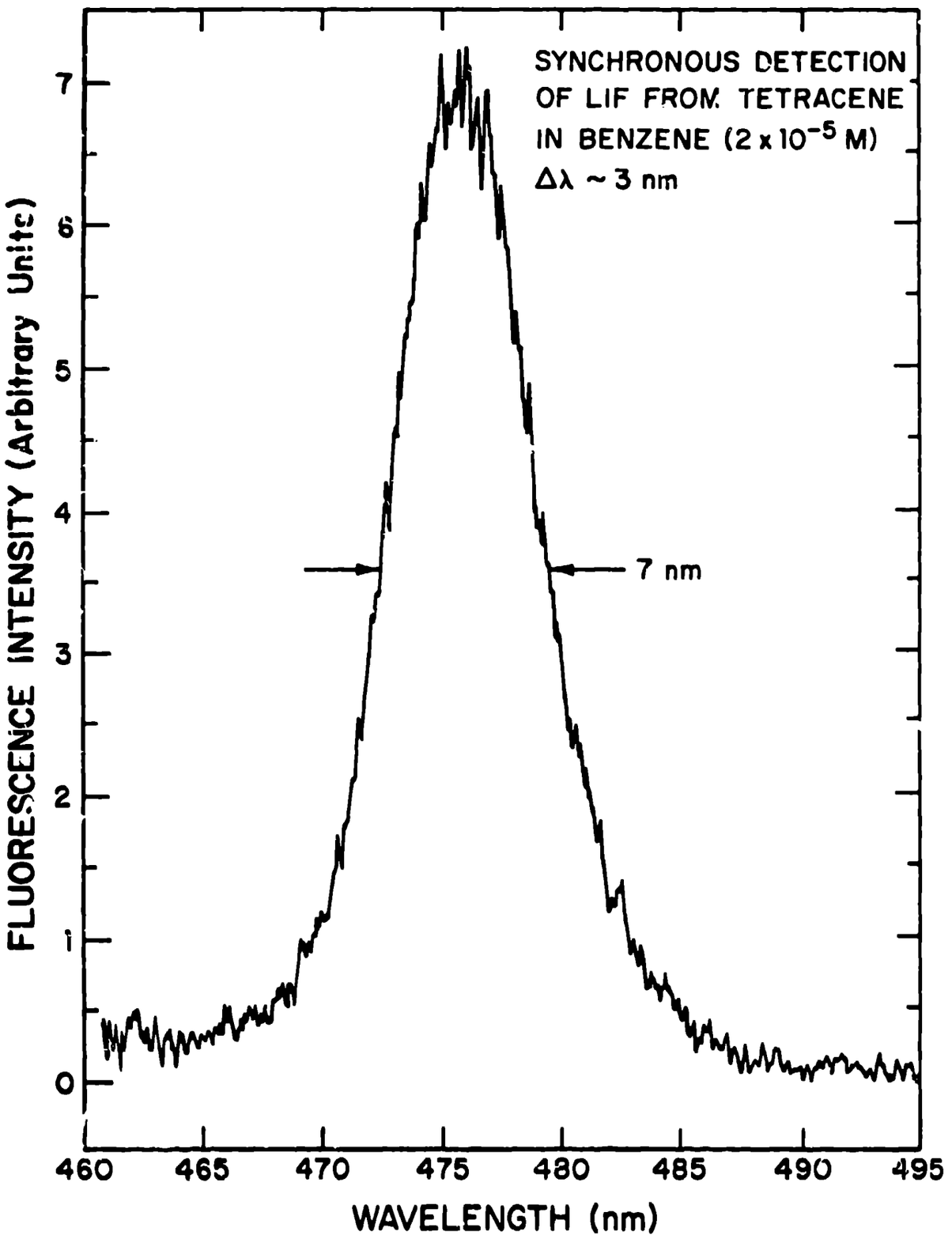

FIGURE 13. SYNCHRONOUS DETECTION OF LASER-INDUCED FLUORESCENCE FROM TETRACENE. The synchronous spectrum is seen to be much narrower than the conventional fluorescence emission spectrum.

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