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TITLE: LASER-INDUCED BREAKDOWN SPECTROSCOPY: A TECHNIQUE FOR ATOMIC  
DETECTION AND MOLECULAR IDENTIFICATION

AUTHOR(S): T.R. Loree and L.J. Radziemski

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LASER-INDUCED BREAKDOWN SPECTROSCOPY: A TECHNIQUE FOR ATOMIC DETECTION  
AND MOLECULAR IDENTIFICATION

T. R. Loree and L. J. Radziemski

University of California  
Los Alamos National Laboratory  
Los Alamos, NM 87544

We have been examining the emission spectra from laser-induced breakdown plasmas as a technique for atomic identification. The concept is straightforward and the apparatus simple (see Fig. 1); the plasma is a bright source requiring little subtlety to resolve. By adding time resolution to the detector, one moves from LIBS (Laser-Induced Breakdown Spectroscopy) to TRELIBS (Time-Resolved LIBS) and for most cases gains considerable sensitivity. Our applications have mostly been aimed at the detection of trace constituents. The only previous use of this technique of which we are aware was a measurement of the fuel/air ratios in combustion.<sup>1</sup>

In the laser-power regimes (from threshold to 10 times threshold) we have used, one is dealing with the spectra emitted by singly-ionized and excited neutral atomic species, superimposed on a varying continuum background. Figures 2 and 3 illustrate the time history of the spectrum in what we thought were pure samples of  $N_2$  and  $O_2$ . The laser pump pulse lasted 80 ns. While the shape of the underlying continuum curve is more a reflection of the silicon diode response than the continuum spectrum, it is clear that the white light dies quickly after the laser pump pulse stops. Both examples also show clearly that the early spectral lines are almost purely ionic, but these also die out in the first microsecond, to be supplanted by atomic neutral lines. The elimination of background improves the contrast ratio of these late-time lines, and in some cases differences in time development cause lines to emerge only at late times. This can be seen in the late appearance of the hydrogen lines in Fig. 3, which came from some unknown hydrogen-bearing impurity in our bottle oxygen.

For sensitivity in the real-time detection of trace elements, TRELIS is the superior technique. In many situations, however, LIBS is adequate and simpler to implement. For example, we used LIBS in field tests designed to detect sodium and potassium in the product stream of a laboratory-scale coal combustor/gasifier.<sup>2</sup> The apparatus used was that of Fig. 1, with detection by a silicon diode array coupled to a Tracor Northern IDARSS system.<sup>3</sup> Figure 4 is a survey spectrum from the gasifier runs and Fig. 5 is a higher-resolution comparison of the sodium D lines (unresolved) as seen from a sample of powdered BYU coal and the gasifier itself. Both alkali metals were easily detected in the gasifier effluent, although an analysis of the ash found only 4.5% Na<sub>2</sub>O and 0.6% K<sub>2</sub>O.<sup>4</sup>

Another promising application of either technique is the identification of organic molecules bearing distinctive atomic species. While fingerprinting of a specific molecule will pose difficulties, classes of molecules (such as organophosphates) may be rapidly detected. As an example of this application, we looked for phosphorus lines from a 0.1" sample of DIMP ((C<sub>3</sub>H<sub>7</sub>)CH<sub>3</sub>PO<sub>3</sub>) in air. A LIBS-generated trio of phosphorus lines is shown in Fig. 6, along with the calculated relative intensities we expected to see.

The enhanced sensitivity afforded by TRELIS is shown in our detection of airborne beryllium compounds. The spectral region of strongest beryllium lines is shown in Fig. 7. The sample vapor was created by moving a block of beryllium into the laser focal spot (in air), then removing the block to an unirradiated portion of the containment cell

while the experiment was carried out. The spectral line at 313.1 nm is interesting on two counts: first, it is the longest-lived ionic line we have seen (by the 1  $\mu$ s delay of this trace, most ionic lines have died out, but this one persists for more than 10  $\mu$ s...see Fig. 8); and second, the dip in the center of the line indicates self-absorption in the cooler envelope of the plasma. In Fig. 8, we show the time development of this particular line. The self-absorption is quite strong at the first two delays, and the third is still suspect. The last two time delays show both the extremely long-lived character of this ionic line and the late-time sharpening of lines that normally occurs as the electron density diminishes.

The use of TRELIBS for real-time monitoring of airborne beryllium shown in Figs. 9 and 10. In both cases the block was irradiated, moved out of the beam as quickly as possible, and then the detection sweep begun. In Fig. 9 the air in the cell was unstirred, resulting in the large signal at early times from a high local concentration. This gradually fell to a steady-state level as the plasma shocks dispersed the sample. In Fig. 10 the air was stirred with an internal fan, giving a more constant signal. In both cases, the run was terminated by pumping on one end of the cell and admitting air to the other end, effectively flushing out the beryllium. The signal response to this action was sensibly instantaneous.

The laser ablation technique put a very small mass of beryllium into the air, but it is difficult to estimate just how small that sample was. Various approaches were tried (thermodynamic, photon numbers and surface work function, etc.) and resulted in estimates of the beryllium

mass in the plasma ranging from picograms to nanograms. This issue was further confused by trials in which the cell, after some usage, was taken apart, washed, reassembled, pumped out, and then filled with air. After a short time the 313.1 nm line reappeared again in the ostensibly clean cell, but would disappear if the cell were flushed with fresh air. The amount of beryllium that would be re-emitted off the walls of the cell under these conditions is not felt to be large.

Our aim was to develop real-time techniques for atomic detection with reasonable sensitivity. We are pursuing a very promising approach to this goal, and have demonstrated real-time results under difficult field conditions. Our sensitivities have surpassed our present ability to measure them, which is gratifying but will lead to a great deal more work. While we had mainly intended to address applications to hostile environments that required non-invasive techniques, it is apparent that LIBS and TRELBS will be quite useful in more mundane situations.

#### REFERENCES

1. Private communication, R. W. Schmieder, Sandia National Laboratories, Livermore, CA 94550.
2. Run by Prof. Paul Hedman, Chemical Engineering Department, Brigham Young University, Provo, Utah.
3. Intensified Diode Array Rapid Scan Spectrometer, manufactured by Tracor Northern, Inc., 2251 West Beltline Highway, Middleton, WI 53562.
4. Analyzed by United States Geological Survey.

## CAPTIONS

Figure 1: A schematic of the apparatus required to conduct LIBS (as shown) or TRELIBS (by adding a spectral detector with time resolution). The particular setup shown was used in our coal gasifier field tests; many other types of sample cells and detectors have been used.

Figure 2: The spectrum generated in an atmospheric pressure  $N_2$  sample at various time delays. This illustrates the general behavior seen in TRELIBS; at early time ionic lines and continuum dominate, to be replaced by neutral lines of increasing sharpness and contrast at later times.

Figure 3: TRELIBS spectra for an atmosphere of  $O_2$ , nominally 99.9% pure. In addition to the trends seen in the  $N_2$  spectra, the late appearance of hydrogen lines shows how well trace impurities can be seen at late times.

Figure 4: A survey spectrum from the coal gasifier runs, showing the whole wavelength range detectable with the diode array. The desired sodium and potassium lines are among the strongest seen.

Figure 5: A comparison of the sodium D lines as seen in the gasifier runs, ... in a laboratory experiment with a powdered coal sample. The gasifier spectrum is felt to come predominantly from ash particles which contain some four times as much sodium as the coal.

Figure 6: A group of phosphorus lines detected from a sample of the organo-phosphate DIMP. Positive identification was made both by wavelength determinations and a comparison to the calculated intensities shown below.

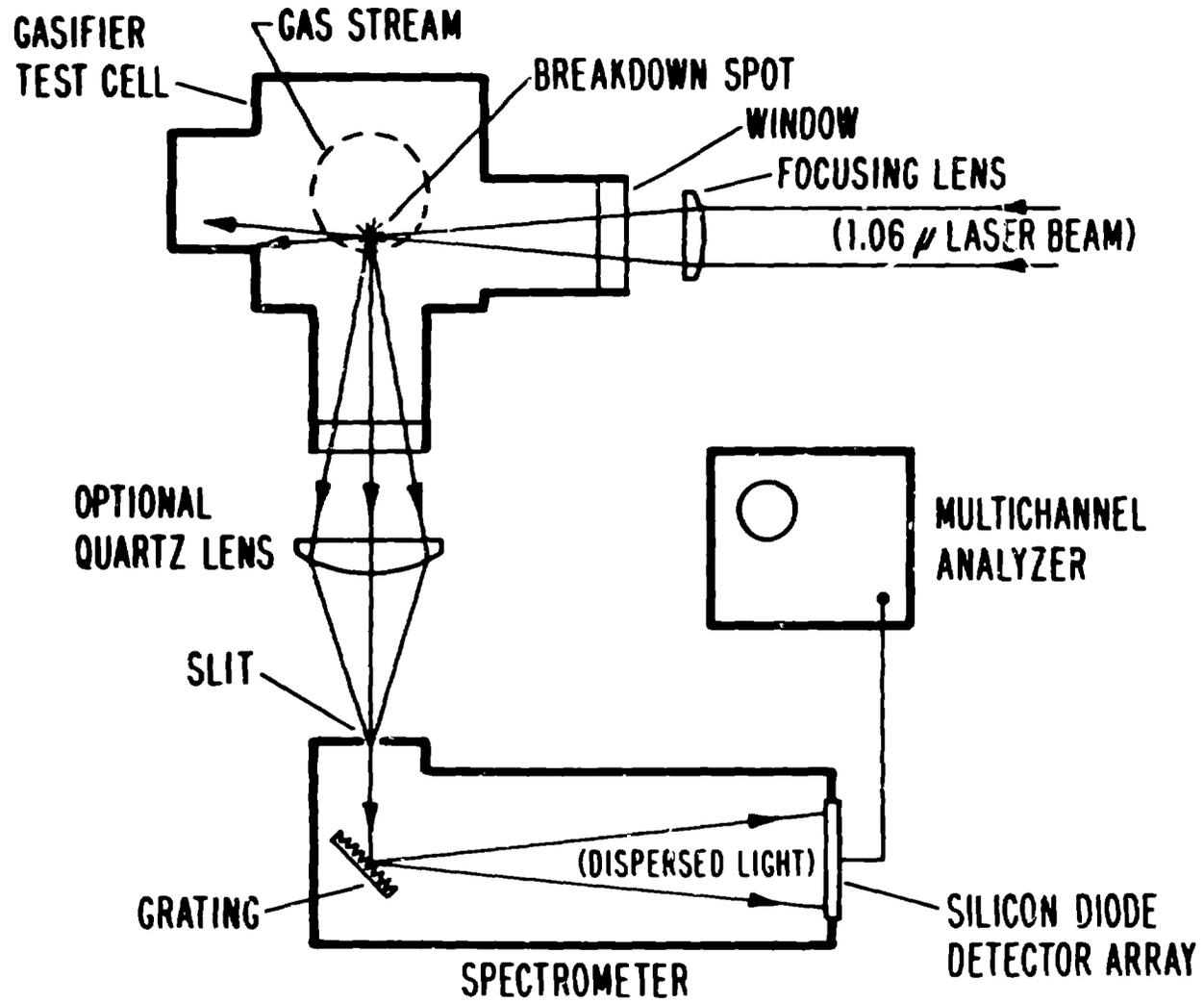
**Figure 7:** The TRELIBS spectrum of beryllium in air at a delay of 1  $\mu$ s. The ionic line at 313.1 exhibits both abnormally long life and a self-absorption dip.

**Figure 8:** A further exploration of the character of the 313.1 nm beryllium line as a function of delay time. Because of the evident self-absorption, it is only at late times that the amplitude of the line reflects the actual concentration of the sample. This is by far the longest-lived ionic line we have seen.

**Figure 9:** An example of monitoring the presence of beryllium in a closed cell. The sample was created by laser ablation shortly before zero time, and is dispersed only by the shock waves of the 10-Hz breakdown. The cell was purged at 55 seconds.

**Figure 10:** As in Fig. 9, but with a internal fan in the cell dispersing the beryllium vapor. The purging of the cell at 65 seconds was again reflected by the diminution of the signal.

# LIBS APPARATUS - BYU CONFIGURATION



AP-1-VG-6073

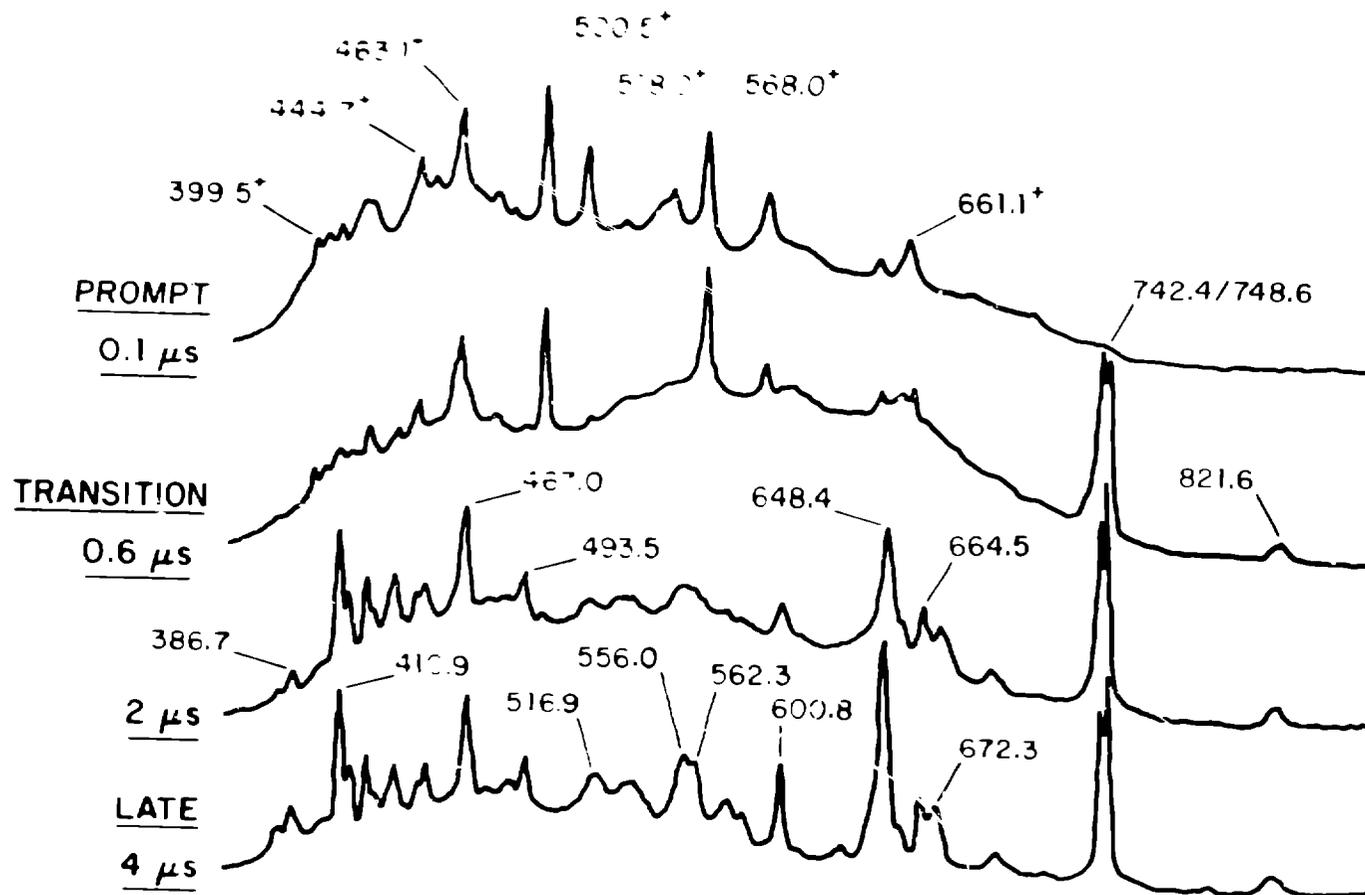


Figure 2

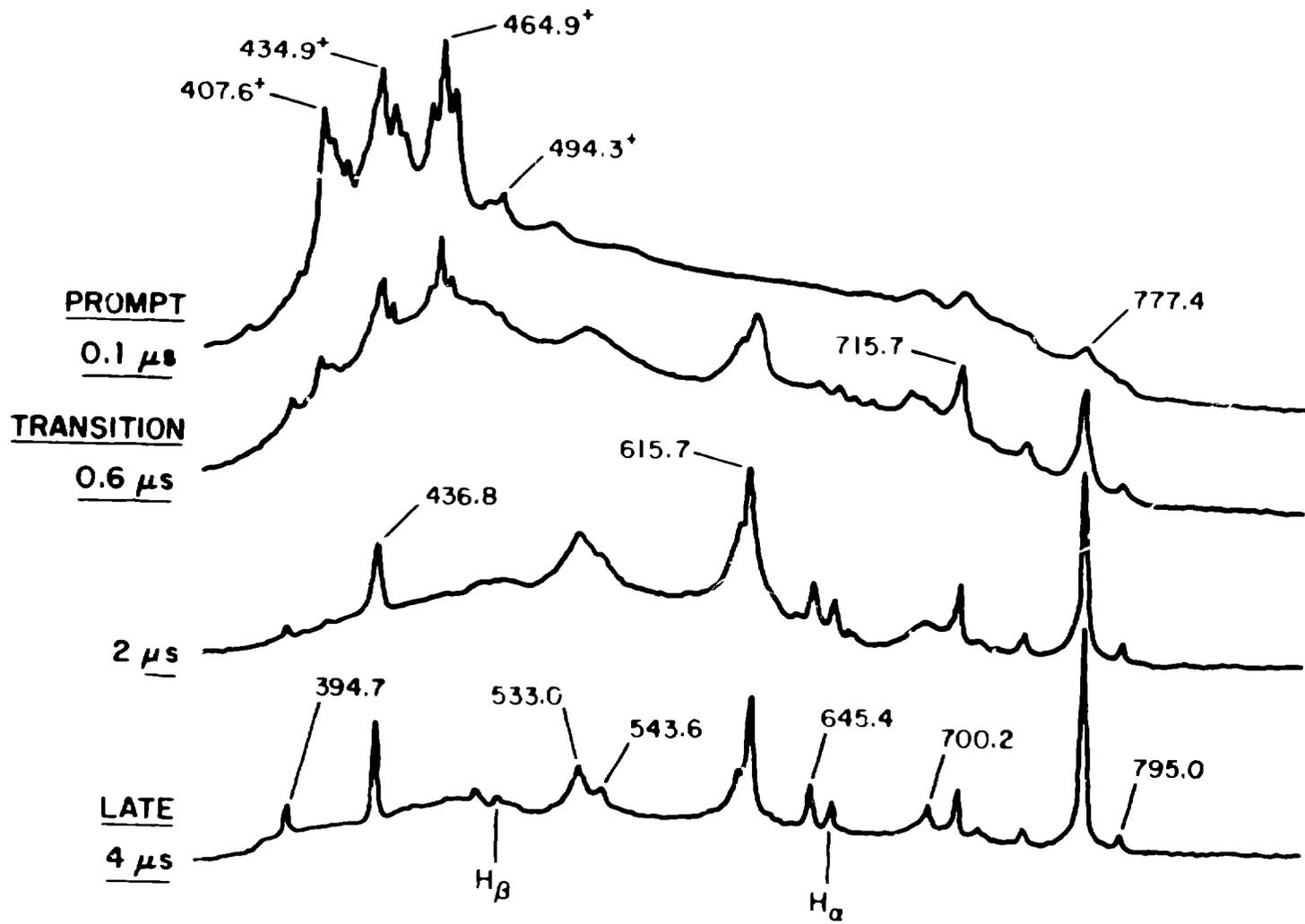
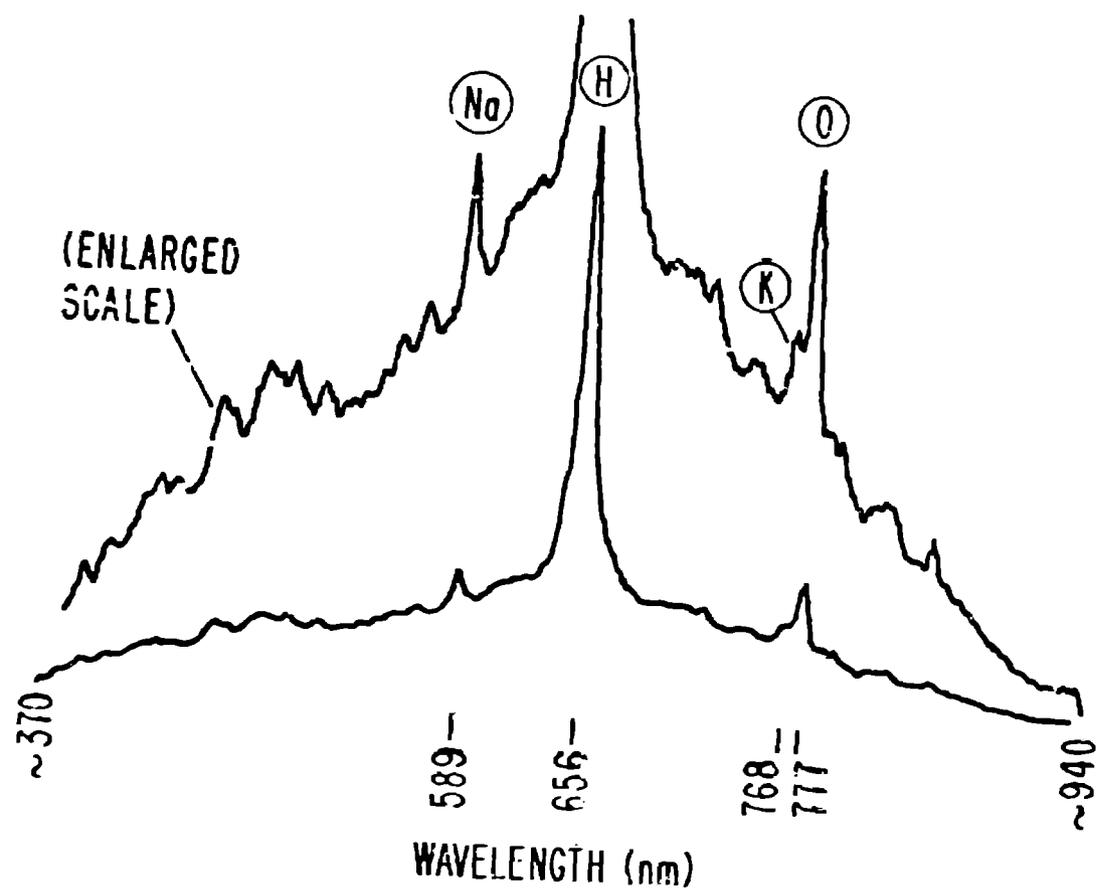
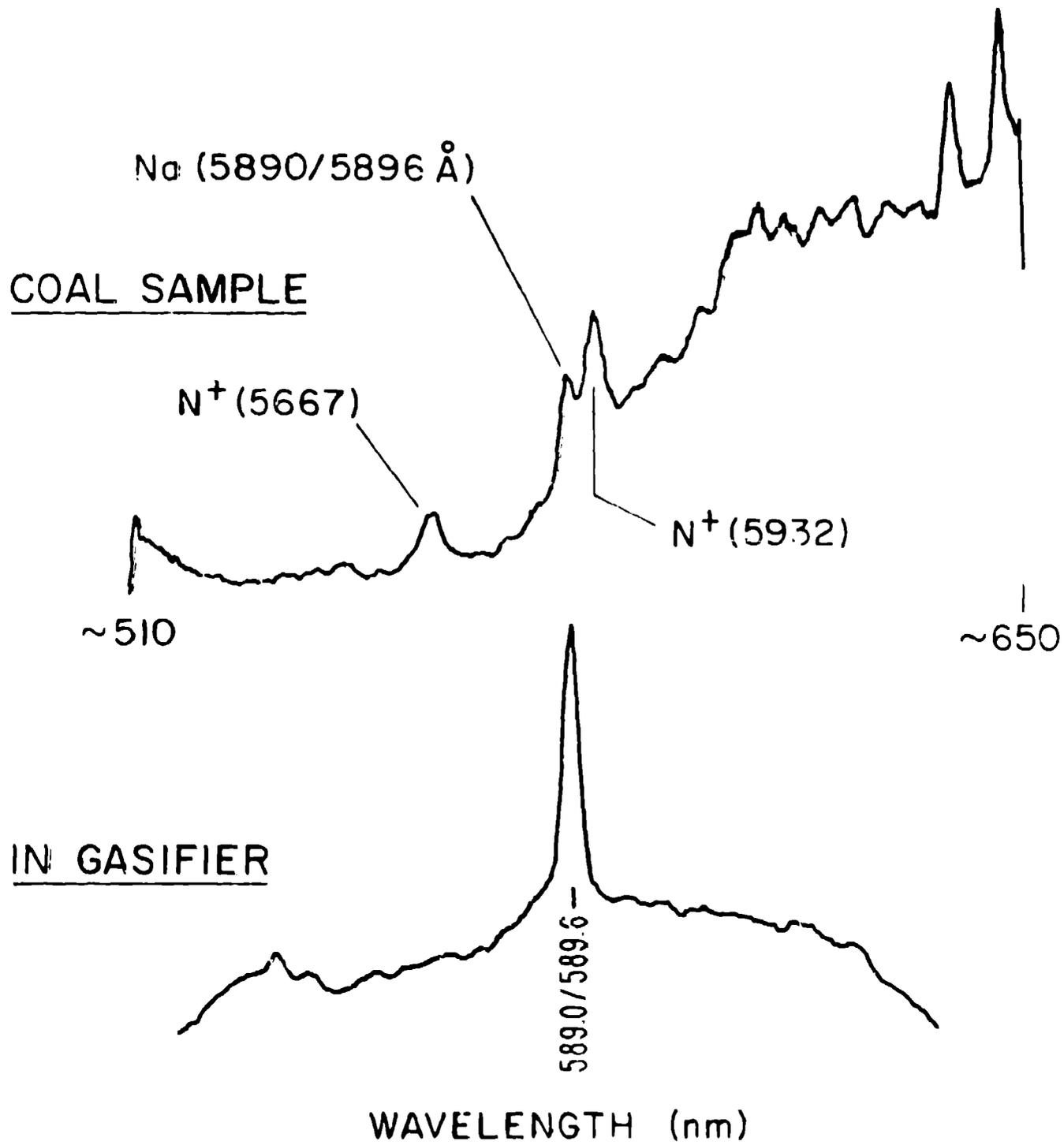


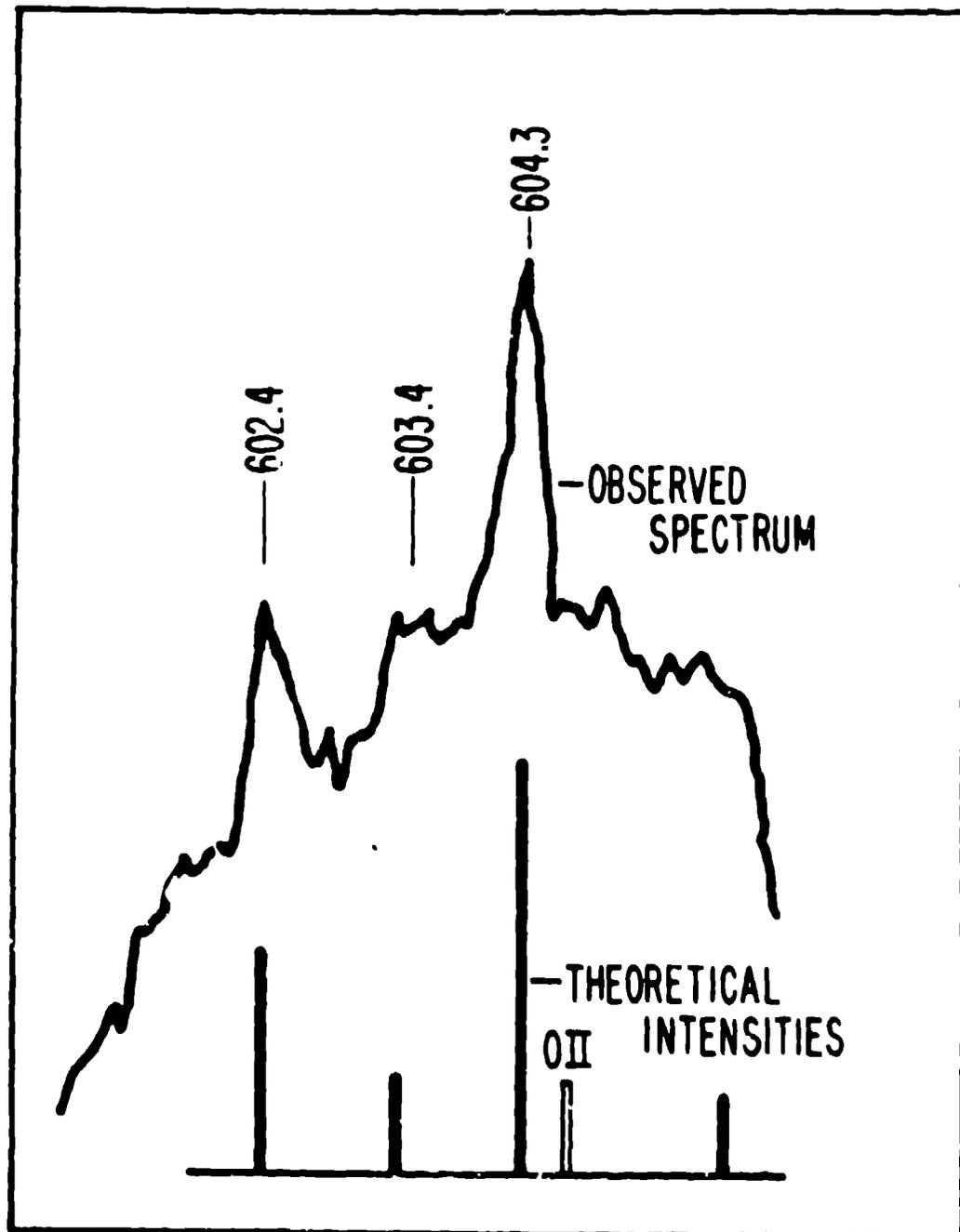
Figure 2



AP-1-VG-6074



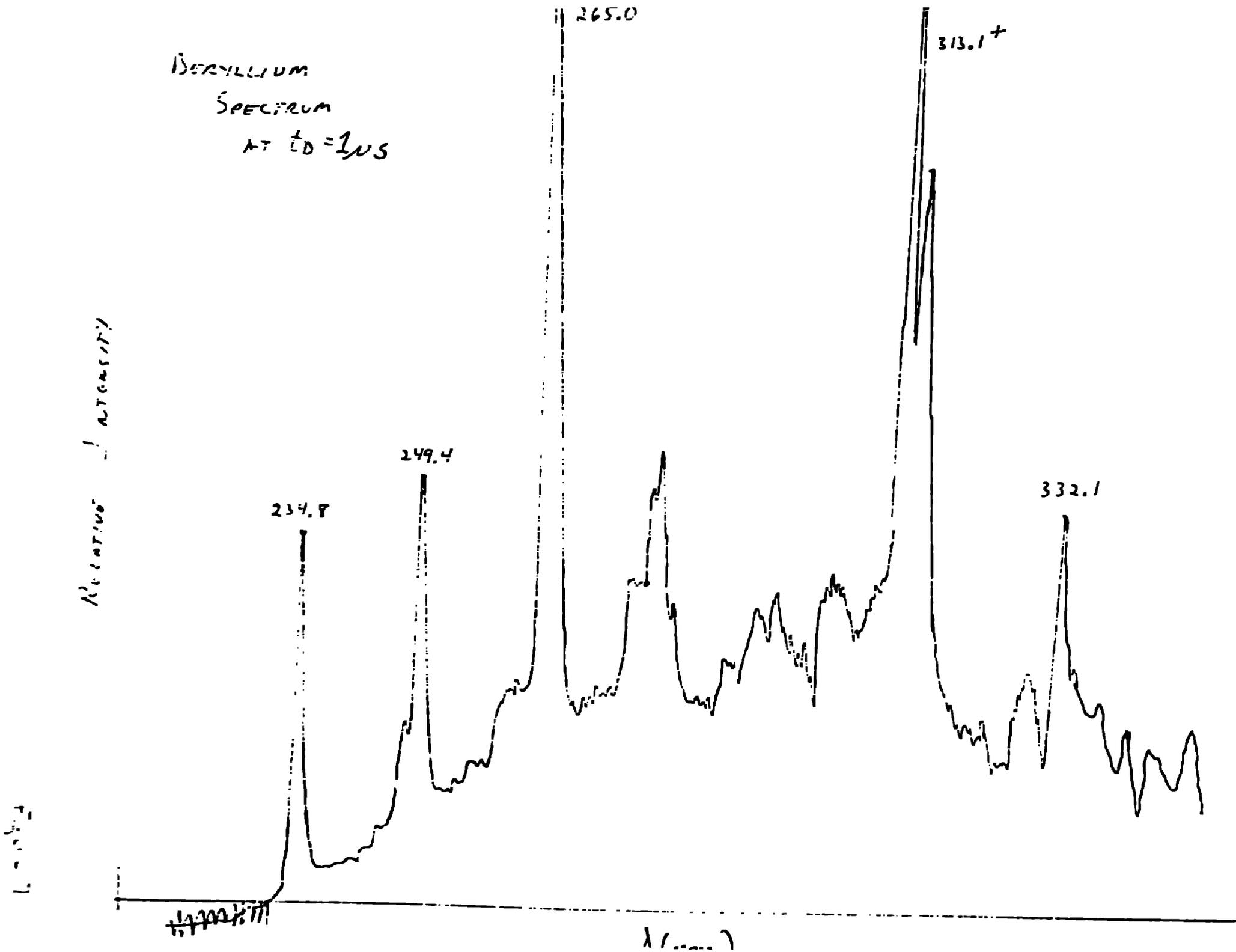
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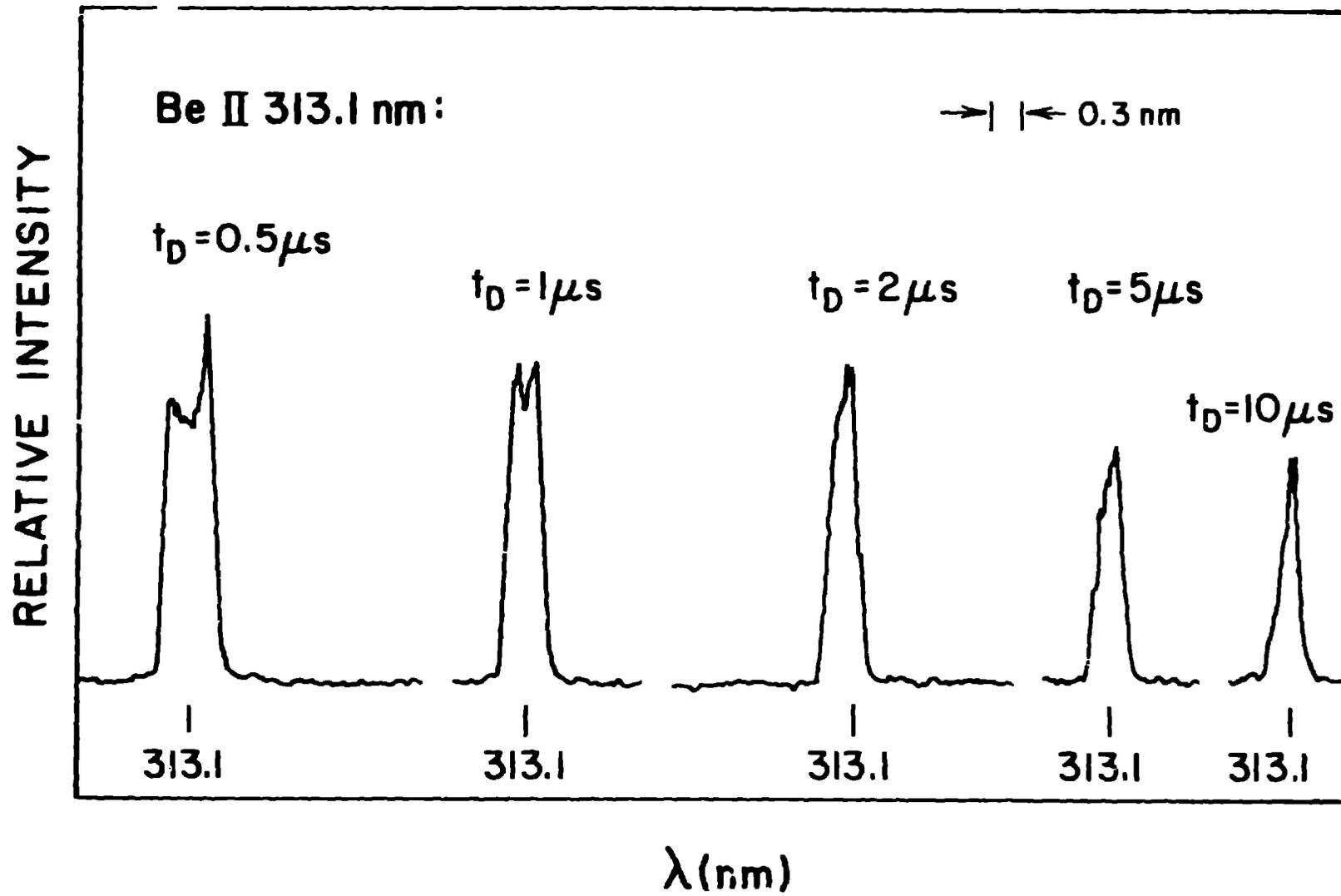


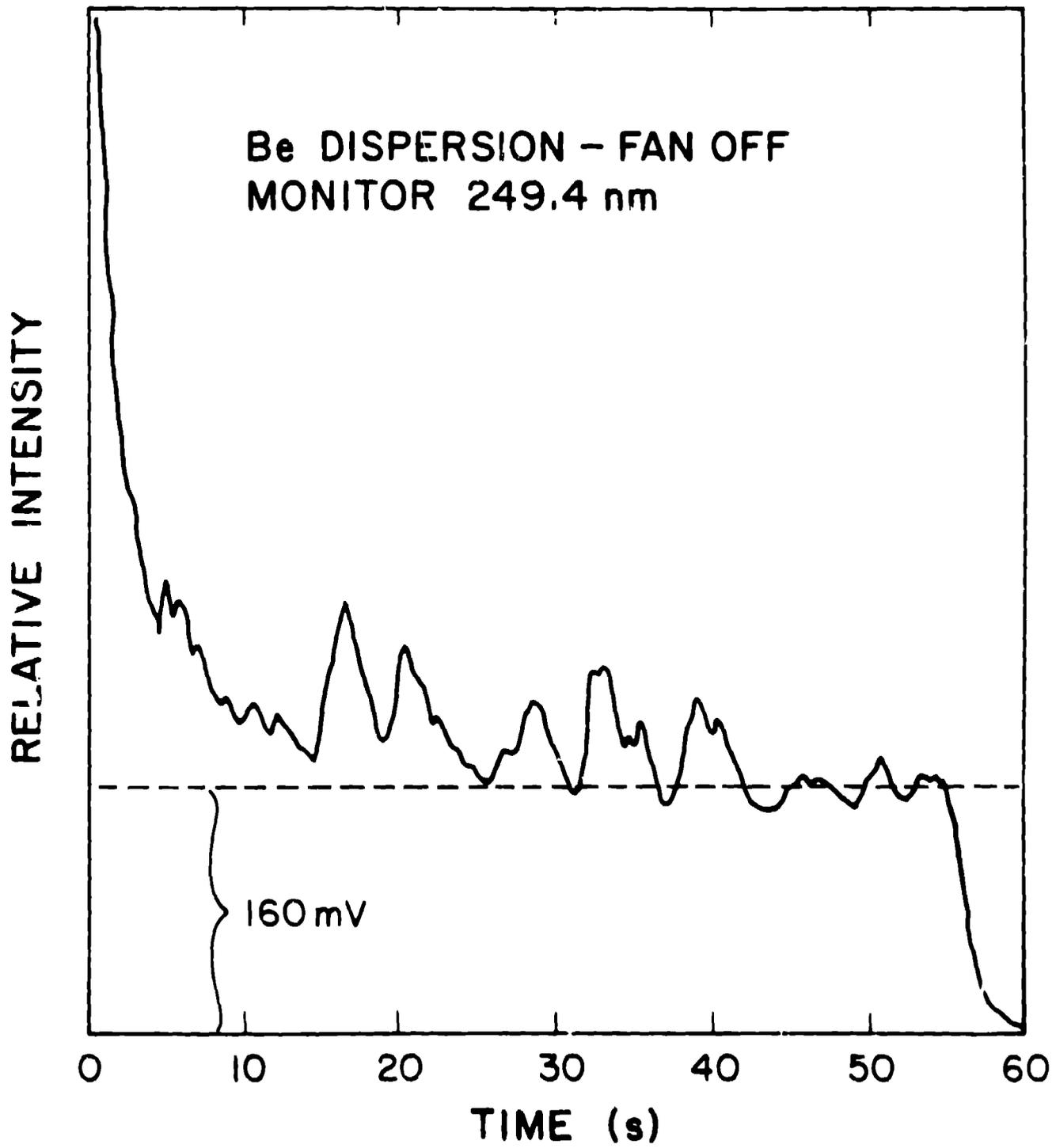
WAVELENGTH (nm)

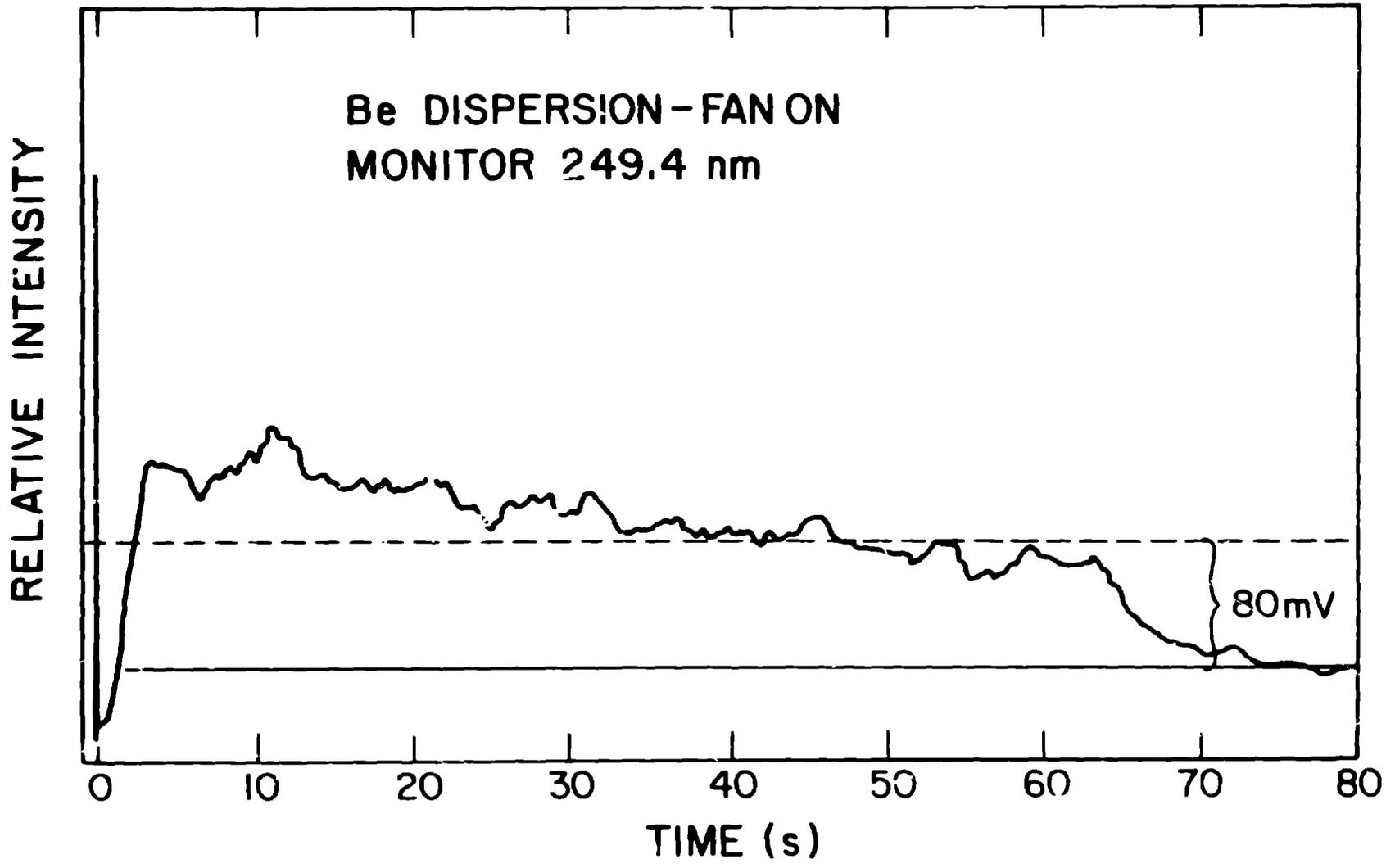
Figure 7

BERYLLIUM  
SPECTRUM  
AT  $t_D = 1 \mu s$









51 April 15