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POTENTIALS AND PROBLEMS

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# ICP-FTS: A NEW ANALYTICAL TOOL ?
# POTENTIALS AND PROBLEMS

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## ABSTRACT

Many new sources and spectrometers have been developed in the ongoing effort to improve multielement analysis by analytical atomic emission spectroscopy. Currently several different laboratories are exploring applications of Fourier transform spectrometry in the ultraviolet and visible spectral regions, especially in conjunction with the inductively coupled plasma source. As a multiplex technique, Fourier transform spectrometry has many characteristics which are unique and significantly different from wavelength dispersive spectrometry. These characteristics offer both potentials and problems for the development of ICP-FTS as a new analytical tool. Examples from research in this laboratory are used to illustrate and discuss these points.

## 1. INTRODUCTION

With multielement analysis as its major objective, analytical atomic spectroscopy might be described as a continual search for the ideal source and the ideal spectrometer. Although many researchers have pointed out that the inductively coupled plasma (ICP) is not an "ideal" source, it has been accepted over the last decade as an extremely workable and effective source and is the current method of choice for multielement analysis in most contemporary analytical laboratories. The "ideal" spectrometer might be described as possessing the following characteristics: wide total spectral range, simultaneous and comprehensive wavelength coverage over any selected bandpass of the spectral range, accuracy of wavelengths, accuracy and linearity of intensities, large dynamic range, variable resolution up to the limit of full resolution of the physical line widths in the source, good sensitivity, fast data acquisition, ease of operation, and reasonable cost. The search for the "ideal" spectrometer has historically included the development and application of spectrographs, monochromators, polychromators, photodiode array spectrometers, and mass spectrometers (ICP-MS). Each of these types of spectrometer has met some of the ideal criteria and had unique advantages, but each has also had its own characteristic set of limitations. Now several laboratories are investigating the possibility of applying Fourier transform spectrometers to spectrochemical measurements in the ultraviolet and visible spectral regions [1-9]. And the question arises: will ICP-FTS prove to be a useful new analytical tool and what are its potentials and problems ?

## 2. THEORY

A Fourier transform spectrometer is a multiplex spectrometer, based on the design and operational principles of a Michelson interferometer, as shown in Figure 1. Light from the source (ICP) enters the aperture of the spectrometer and is collimated. A beamsplitter divides the beam into two parts which travel the two arms of the interferometer, are reflected by mirrors back to the beamsplitter and recombined. The recombined beam is focused onto a single multiplex detector. The signal at the detector is a sum of the interference of all the wavelengths present in the two recombined beams. If one or both of the mirrors move so that the optical paths in both arms are not equal, then constructive and destructive interference will occur according to the optical path difference and the wavelengths of light. If the mirrors move as a function of time, then the time-dependent signal at the detector will be a record of the changing interference effects of all the wavelengths present, called an interferogram. The interferogram is the time-domain half of a Fourier transform pair, and the mathematical process of Fourier transformation performed by a digital computer produces the frequency-domain half of the pair, known more familiarly as the spectrum. At no point in the process is the light physically separated into component wavelengths as in wavelength-dispersive systems using prisms or gratings. The Fourier transform spectrometer acts as the multiplexing device to encode the independent pieces of information (intensities of all the wavelengths of light in the source) into a form which can be simultanously detected by a single detector. The computer acts as the device to decode the multiplexed information back into unique and independent pieces of information (the spectrum). The principles of Fourier transform spectrometers and the Fourier transform process have been previously described in detail [10-14].

## 3. EXPERIMENTAL

Over the past four years, studies at this laboratory have investigated the ICP as a source for high resolution Fourier transform spectroscopy. These studies have included an assessment of the analytical applicability of ICP-FTS [1,15], a vertical profile of Fe excitation temperatures in the ICP [16], line width and line shape analysis of Fe I in the ICP [17], ICP argon emission in the near IR [18], and population distributions and oscillator strength values for Mo I in the ICP [19]. These studies were performed using the one-meter Fourier transform spectrometer in the McMath solar telescope at the National Solar Observatory at Kitt Peak, Arizona, and the experimental details have been described in those previous publications. This laboratory is currently engaged in building a state-of-the-art Fourier transform spectrometer [20] for applications in the ultraviolet, visible, and infrared to far infrared spectral regions. As part of a national facility for high resolution spectroscopy, this instrument will serve many functions in basic and applied chemistry, physics, and materials science, including continuing studies focused at the development of new and advanced techniques in analytical chemistry. The specifications of the Los Alamos Fourier tranform spectrometer, expected to be completed in 1986, are given in Table 1.

## 4. DISCUSSION

### 4.1 Potentials

The most outstanding potentials of ICP-FTS as an analytical tool are (1) the simultaneous and comprehensive wavelength coverage of the selected bandpass (2) the ability to achieve high resolution relatively easily in a compact instrumental system, and (3) the high degree of accuracy of both wavelength and intensity measurements.

A Fourier transform spectrometer simultaneously records all the spectral information within the selected bandpass so that the transformed spectrum includes all the emission lines from atomic and molecular species in the source as well as all the background and baseline characteristics. The bandpass is determined by the combination of selected optical and electronic filters and components and detector response. This bandpass may be as small as a few, or as large as several hundred, nanometers. The total spectral information within that selected bandpass is completely recorded and permanently available at any time in the interferogram or the transformed spectrum. Unlike wavelength-dispersive systems such as the polychromator or monochromator which require that only a few wavelengths be preselected, Fourier transform systems allow the selection of the wavelengths for analysis to be performed at any time after the spectrum has been recorded. Thus the selection can be based on the examination and content of actual spectrum, and the maximum flexibility of choice is allowed.

Total qualitative analysis is therefore inherently achieved since the comprehensive emission spectrum of all species in the source will be recorded within the selected bandpass. Spectral interferences are more easily identified since the presence of key lines of analytes will alert the analyst to possible interferences at other wavelengths. Computerized cross-reference wavelength tables can be used for initial qualitative analysis as well as for flagging potential spectral interferences. Alternate line selection in the case of spectral interferences is available since all the emission lines of the analyte of interest will be present in the spectrum. The computer system can cross-reference potential spectral interferences based on the initial qualitative survey and suggest the best interference-free lines to be used for the analysis. Since all the spectal information is available, it is also possible to use more than one emission line of a given species for quantitative analysis. "Multiple line analysis" might be used to sum weighted intensities of several lines of an element, based on a reference spectrum, in order to increase sensitivity. The comprehensive wavelength coverage is also an invaluable asset in the case of spectrophysical studies of the ICP for which large data sets are required such as temperature determinations [16] and population distribution and oscillator strength measurements [19]. Figure 2 shows a portion of an ICP-FTS spectrum of a multielement solution, demonstrating the comprehensive wavelength coverage. Argon lines from the ICP plasma gas are also present.

Compared to wavelength-dispersive spectrometers, it is relatively easy to achieve high resolution in a very compact instrumental system based on an interferometer [6]. The resolution of the resulting spectrum is determined by the maximum optical path difference (OPD), or the extent of the movement of the mirrors, in the interferometer [10-14]. The greater the optical path difference attained in recording the interferogram, the higher the resolution in the transformed spectrum. In the unapodized case, the resolution R (in wavenumbers) is equal to the inverse of two times the maximum optical path difference L (in cm):

$$R = 1/2L \qquad (1)$$

The resolution will be constant across the spectrum in wavenumber units, but will vary as a function of wavelength. Table 2 shows how the resolution varies in wavelength units for a fixed OPD of one meter. Long path differences (large interferometers) are required to achieve high resolution in the infrared. Much more compact systems are sufficient for high resolution in the visible and ultraviolet. Table 3 gives some values of resolution (both in wavenumbers and in wavelength at 300 nm) as a function of OPD. High resolution for the UV-VIS is attained with relatively small optical paths compared to wavelength-dispersive instruments. Figure 3 is a portion of the multielement spectrum from Figure 2, showing the high resolution actually achieved in the FTS spectrum.

A conservative rule of thumb [11] states that if the physical line width is three times greater than the FTS resolution, then the instrumental effect on the observed line width is less than 0.1%, which is essentially negligible. On the other hand, low FTS resolution results in a distinct instrumental line shape or resolution function for the spectral lines [10-14]. The resulting instrumental line shapes are due to the Fourier transform process and are mathematically described as sinc functions. There are severe side lobes or "ringing" of positive and negative intensities on each side of the spectral line. For adjacent lines, these side lobes are additive and may produce erroneous intensity values for the analytical lines or may obscure less intense spectral information. These side lobes can be greatly reduced by a treatment of the interferogram called apodization [10-14,21], which produces an instrumental function with much less pronounced side lobes, but which also increases the width of the instrumental function and further decreases the resolution for a given optical path difference. Figures 4 and 5 illustrate a portion of the vanadium spectrum recorded at both low and high resolution to demonstrate this point. The low resolution example is completely unapodized and shows the most extreme case of under-resolved ringing. The high resolution case shows full resolution of the physical line widths and shapes, and reveals the presence of an additional spectral line of vanadium which was obscured by ringing in the low resolution case.

Previous studies of the ICP using a high resolution Fourier transform spectrometer have reported on the line widths and line shapes of Fe I in the ICP [17]. Emission line widths depend on several factors including the temperature of the source, the atomic weight of the element, and the wavelength of the transition. Table 4 presents a survey of measured line widths for both atom and ion lines of several different elements over a wavelength range in the UV-VIS. Using the factor of three rule of thumb stated above, the table also shows the calculated optical path difference required to fully resolve these lines. For most medium weight elements, an OPD of 5-6 cm will provide full resolution. For the heavier elements such as the rare earths and actinides, an OPD up to 14 cm is required due to the narrower line widths.

If resolution is sufficiently high to fully resolve the physical line widths in the source, then spectral interferences will be reduced to the natural line widths, without any significant effects due to instrumental line broadening. In this case, spectral interferences will be greatly reduced in number for any given analysis problem, and analyses involving very complex spectra such as those generated by the rare earths and actinides will be simplified, perhaps even eliminating some time-consuming sample pretreatment and chemical separation steps now necessary for those analyses. Figure 6 shows an example of the utility of high resolution in the analysis of iron in a uranium matrix. At low or medium resolution, the density and complexity of the uranium matrix emission would interfere prohibitively with the analysis of iron, but at high resolution it is possible to select analytical lines for iron with no uranium interference at all.

High resolution is also extremely desirable for applications of FTS to spectrophysical studies. The ability to measure line widths and line shapes provides information for the study of excitation and energy transfer mechanisms in the source. Also high resolution can be applied to the study and measurement of hyperfine structure and isotope shifts as well as to isotope abundance measurements, especially in nuclear chemistry applications.

The third major potential advantage of ICP-FTS is the high degree of accuracy of both the wavelength and relative intensity measurements. Only a single internal laser reference wavelength is required to set the entire wavelength scale for the spectrum. With reasonable care and good FTS instrumentation, the wavelength accuracy for high and moderate strength lines can be as good as 0.001 $cm^{-1}$ ($9X10^{-6}$ nm at 300 nm) or better. Accuracy of this quality is very beneficial to both qualitative and quantitative analysis and is especially useful for the application of new approaches to data treatment such as multiple line analysis or correlation techniques which depend on accurate and reproducible wavelength measurements.

Intensity measurements are also accurate and linear by FTS. Since the whole spectrum is recorded simultaneously, it is a relatively easy procedure to perform instrument intensity calibrations based on intensity standards and correct the relative intensities of the the whole spectrum for instrumental response due to the optics, filters, detectors, etc. These corrected relative intensities, combined with the accuracy of the wavelengths, can be very valuable for spectrophysical studies such as temperature determinations or population distributions.

An obvious application for ICP-FTS which combines all three major potentials is the production of a new set of standard wavelength tables for ICP emission of the elements. The ability to comprehensively measure the entire spectrum (quite feasibly from 180nm to 1.1 μm) at full resolution of the physical line widths and with very high accuracy of wavelengths and corrected relative intensities across the entire spectrum is unique to ICP-FTS. These standard reference wavelength tables could provide a valuable resource to the ICP-user community. If these tables were computer-based, then spectral identification and cross-referencing for spectral interferences could be easily programmed into any ICP-user system, whether FTS or wavelength-dispersive. Furthermore, if the tables are produced at full resolution, it would be possible for users of lower resolution instruments to program a calculation to generate tables based on their own instrumental function and to predict spectral interferences which will occur due to instrumental broadening on these systems. Some preliminary work on the production of such tables has been completed [17,18,22].

### 4.2 Problems

The problems to be faced in developing ICP-FTS as a new analytical tool are essentially the same factors which have been responsible for the slower development of FTS in the ultraviolet and visible compared to the rapid development over the past decade of FTS for the infrared (FTIR). These problems include: (1) more stringent optical and mechanical tolerances are required for interferometry at the shorter wavelengths (2) limitations in free spectral range may result in aliasing of the transformed spectra and (3) the multiplex advantage may actually be replaced by a multiplex disadvantage in the UV-VIS, degrading detection limits in some analytical applications.

Because FTS depends on the interference effects of the recombined light beams, the mechanical and optical tolerances for instrument design, construction, and operation become much more severe at the short wavelengths of the visible and ultraviolet, even requiring current state-of-the-art technology. The normal requirement is that the recombined beams be plane and parallel to within $\lambda/4$ of the shortest wavelength of interest [6]. This requirement forces strict specifications on all the optical surfaces of the interferometer and also on the mechanical movement and control of the mirrors, which must be accurately positioned to within a few angstroms [20]. Also the criteria for the digitizing electronics are very strict in order to achieve high accuracies in the intensities [20]. All these factors make design and construction of Fourier transform spectrometers for the UV-VIS very challenging [2,6-9,20].

The free spectral range [10-14] of an FTS spectrum is that range of wavenumbers, theoretically extending from zero wavenumbers to some finite upper limit (from infinite wavelength to some finite short wavelength limit), which can be accurately recovered from the recorded interferogram without aliasing of the transformed spectrum. The free spectral range FSR (in $cm^{-1}$) is determined by the sampling interval S (in cm of optical path difference) of the interferogram:

$$FSR = 1/2S. \qquad (2)$$

In order to digitize the interferogram (the time-dependent signal at the multiplex detector of the interferometer) for the discrete fast Fourier transform, the interferogram is sampled at repetitive equally-spaced intervals. The simplest way to reproducibly fix these intervals is by using a reference laser following an independent but simultaneous path through the interferometer to a reference detector (see Figure 1) and sampling the interferogram on each cycle of the laser frequency modulation. For a helium-neon reference laser frequency of .6328 μm, the resulting free spectral range will be 7901 $cm^{-1}$ (1.2656 μm). This means that the shortest wavelength in the spectrum which can be observed without aliasing is 1.27 μm. Spectrochemical measurements for analytical atomic spectroscopy require observation of wavelengths in the ultraviolet and visible, preferably to wavelengths as short as 180 nm. In order to observe these spectra without aliasing, the sampling interval of the interferogram must be much smaller. Table 5 shows the sampling interval, free spectral range ($cm^{-1}$), and short wavelength limit for unaliased spectra based on simple subdivisions of the helium-neon laser frequency. Methods of achieving smaller sampling intervals include: subdivision of the HeNe laser frequency by frequency doubling techniques or multiple optical passing in the interferometer, or by phase locking a Zeeman-split HeNe laser to control the mirror drive servo system. These techniques are all feasible (and the latter approach is used in both the Kitt Peak and Los Alamos instruments [20]), but they do add complexity and cost to the instrumental design. The alternative approach is to accept aliasing of the spectra.

Aliasing [10-14,23] is the phenomenon of overlapping of spectral replicas resulting from the mathematical Fourier transform of the interferogram to the spectrum. It is a property of the FT process [11-13] that the transformed spectrum will consist of both a positive and a negative image, symmetric about zero on the wavenumber axis. Further, for a given sampling interval S, both these images will be replicated along the wavenumber axis at intervals of 1/S. The transformed spectrum will consist of all replicas of both images, and it is not possible to distinquish whether a line in the transformed spectrum originated from a positive or negative image or its replica. Therefore, any spectral information at a wavenumber greater than the free spectral range (1/2S) will overlap or be aliased into the free spectral range with the apparent result that high frequency information is "folded over" into the low frequency region of the spectrum. This is illustrated in Figure 7.

Aliasing may be prevented by either (1) selecting or filtering the original spectral source so that no information is contained above the free spectral range limit or (2) controlling the sampling interval of the interferogram so that the free spectral range is great enough (the sampling interval is small enough) to contain all the spectral information present in the source.

Aliasing is a precise phenomenon. With a known sampling interval, the free spectral range and the replication intervals are precisely known. All the true spectral information from the source is now represented in the free spectral range from 0 to 1/2S $cm^{-1}$, and each further interval of 1/2S $cm^{-1}$ in the transformed spectrum simply contains duplications of that information. However, it is impossible to determine from which interval a given spectral line in the observed spectrum originates. That means that in the case of an unknown spectrum (such as the analysis of a sample of unknown composition), the wavenumber assignments of the lines in an aliased spectrum are not unambiguous or simply sequential. The wavenumber axis across the free spectral range is actually fan-folded in intervals of 1/2S, and each observed line may have more than one (precise, but not unique) possible value. A further disadvantage of aliasing is that due to the additive overlapping of the replicas, the potential for spectral interferences is increased (especially at low resolution) and the baseline noise from the overlapping intervals is also additive, decreasing the analytical sensitivity of the resulting spectrum. The advantages of aliasing relate to the use of less computer memory to store the interferogram or the spectrum and less computer time to perform the Fourier transform. If the number of data points to be recorded in the interferogram is fixed or limited by available computer memory, then aliasing can be used to attain higher resolution in the resulting spectrum. Similarly, for a given resolution, fewer data points are required to generate the aliased spectrum than the unaliased spectrum.

Whereas the realization of the multiplex advantage was a major impetus in the development of FTIR, the application of FTS in the UV-VIS may actually involve a multiplex disadvantage which must be considered carefully in evaluation of ICP-FTS as a new analytical tool. The multiplex advantage is a gain in signal-to-noise ratio of the spectrum compared to that achieved for comparable measurement time by a sequential scanning wavelength dispersive spectrometer. It is realized in detector noise limited situations (such as commonly occur in the infrared spectral region): the noise at the detector is independent of the signal intensity. UV-VIS measurement situations are usually photon or source noise limited: the noise at the detector increases in proportion to the signal intensity. Since FTS is a multiplex technique, all the source emission intensity is simultaneously recorded by a single detector. In the FT process, the noise from all wavelengths in the source is distributed throughout the resulting spectrum. The characterization of noise in the FTS spectrum is an important subject of study in the development of analytical ICP-FTS [1,24]. One implication is that noise from strong emission lines in the source may increase the overall baseline noise of the transformed spectrum and thereby degrade the detection limits for other analytical species in the sample. In order to evaluate the possible extent of this multiplex disadvantage in analytical applications, studies were performed in this laboratory to approximate a "worse case" situation. The results of this study have been previously reported [1] and demonstrated that matrix elements such as the alkaline earths, which exhibit intense emission in a few spectral lines, can produce a serious degradation of detection limits even at relatively low concentration levels in the sample while matrix elements of the transition-type elements such as iron and nickel have only moderate effects on detection limits for other analytes even when present at moderate concentration levels in the sample. The conclusion is that the multiplex disadvantage can be a serious problem in the use of ICP-FTS as an analytical tool and must be given careful consideration and further study in the development of analytical techniques based on ICP-FTS. Unlike ICP-MS, ICP-FTS does not promise major breakthroughs in the frontier of sensitivity. Even under optimized conditions, detection limits for ICP-FTS will probably be comparable to, but not significantly better than, those attained by wavelength dispersive systems. The impetus behind the development of analytical ICP-FTS lies in its other unique potentials.

## 5. RESEARCH POTENTIALS

As with any new direction of scientific development, the field of ICP-FTS is rich in potential for research and investigation. Any development which reduces the noise in the source will reduce the detrimental effects of the multiplex disadvantage and improve analytical sensitivity. This may include new designs for torches and nebulizers in general or especially for FTS applications [25]. New methods of sample introduction will be needed, either to reduce source noise due to the nebulization process, or to find ways to introduce solid samples for ICP analysis with the steady state signal required by the FTS.

It may be that the worse case of multiplex disadvantage, in which intense matrix emission is localized in a few spectral lines, may actually be the simplest to solve by optical filtering: either the undesired matrix emission may be notch filtered out, or the desired analytical lines may be narrow band filtered in. This may be accomplished in some cases by simple optical filters. Other more complex cases may necessitate predispersion, postdispersion with multiple detectors, or some combination of both. One such approach called "windowed slew scanning" has been reported [4]. Ideally, one would like a bandpass selector for the FTS which would allow the analyst to select a bandpass of any extent over any range.

The area of data treatment and analysis for analytical ICP-FTS is currently wide open to clever and innovative approaches using, for example, multivariate and correlation techniques in either the Fourier or the spectral domains. Some work in this field has been initiated [26-28].

Another rich potential, now that the utility of FTS in the UV-VIS has been demonstrated, is the development of entirely new excitation sources [29] whose properties may be more suited to the multiplex approach than the ICP.

## 6. CONCLUSIONS

Like all new techniques developed for analytical chemistry, ICP-FTS offers both powerful potentials and unique problems. No new technique ever totally replaces those already in use, but rather provides a complementary method with some new advantages and some inherent limitations. The multiplex approach is relatively unfamiliar in analytical atomic spectroscopy. There is still much research to be done before its implications in analytical chemistry are understood, and there are many unique characteristics to be carefully considered before ICP-FTS becomes a standard tool in the analytical laboratory.

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## TABLE 1

The Los Alamos Fourier Transform Spectrometer.

| | |
|---|---|
| optical path difference | 2.5 meter<br>(5.0 meter double pass) |
| spectral range | 200 nm - 20 μm<br>(50000 - 500 $cm^{-1}$) |
| resolution | 0.002 $cm^{-1}$<br>(0.001 $cm^{-1}$ double pass) |
| optical throughput | 3.5 inch beam diameter |
| intensity accuracy | as good as 0.1% |
| wavenumber accuracy | as good as 0.0001 $cm^{-1}$ |

## TABLE 2

Resolution as a function of wavelength for a fixed optical path difference of one meter.

| λ | R (nm) at λ |
|---|---|
| 200 nm | 0.00002 |
| 500 nm | 0.000125 |
| 1 µm | C.0005 |
| 5 µm | 0.0125 |
| 10 µm | 0.05 |
| 20 µm | 0.2 |

## TABLE 3

Resolution as a function of optical path difference.

| OPD (cm) | R ($cm^{-1}$) | R (nm) at 300 nm |
|---|---|---|
| 0.25 | 2.0 | 0.018 |
| 0.50 | 1.0 | 0.009 |
| 1.00 | 0.5 | 0.0045 |
| 2.50 | 0.2 | 0.0018 |
| 5.00 | 0.1 | 0.0009 |
| 10.00 | 0.05 | 0.00045 |
| 25.00 | 0.02 | 0.00018 |
| 50.00 | 0.01 | 0.00009 |
| 100.00 | 0.005 | 0.000045 |

## TABLE 4

Line widths in the ICP.

| LINE | (nm) | LINE WIDTH | | OPD to RESOLVE LINE WIDTH (cm) |
|---|---|---|---|---|
| | | (nm) | ($cm^{-1}$) | |
| U II | 424.44 | .0020 | .109 | 13.8 |
| Ca I | 422.67 | .0045 | .254 | 5.9 |
| Al I | 396.15 | .0050 | .316 | 4.8 |
| Ba II | 389.18 | .0031 | .206 | 7.3 |
| U II | 378.28 | .0017 | .120 | 12.5 |
| Cr I | 360.53 | .0033 | .254 | 5.9 |
| Fe I | 357.01 | .0030 | .233 | 6.4 |
| Ni I | 352.45 | .0030 | .242 | 6.2 |
| Sr II | 346.45 | .0031 | .259 | 5.8 |
| V II | 327.11 | .0034 | .319 | 4.7 |
| Ca II | 317.93 | .0036 | .356 | 4.2 |

TABLE 5

Free spectral range as a function of sampling interval.

| multiple of HeNe | sampling interval | FSR | short wavelength limit |
|---|---|---|---|
| 1 | 0.6328 μm | 7901 $cm^{-1}$ | 1.2656 μm |
| 1/2 | 0.3164 μm | 15802 $cm^{-1}$ | 0.6328 μm |
| 1/4 | 0.1582 μm | 31604 $cm^{-1}$ | 0.3164 μm |
| 1/8 | 0.0791 μm | 63208 $cm^{-1}$ | 0.1582 μm |

# FIGURE CAPTIONS

Figure 1. Fourier transform spectrometer based on Michelson interferometer.

Figure 2. ICP-FTS spectrum of a multielement solution. A 10 nm segment of the spectrum is shown to illustrate the comprehensive wavelength coverage of Fourier transform spectrometry. Many lines of several different elements are present in this segment. The spectrum is plotted on a wavenumber axis; corresponding wavelengths are indicated on a secondary axis.

Figure 3. ICP-FTS spectrum of multielement solution at high resolution. This is an 0.5 nm segment of the multielement spectrum shown in Figure 1, plotted on an expanded wavenumber axis to illustrate the actual quality of resolution in the spectrum obtained with an optical path difference of 6.4 cm. The incomplete resolution of the Mn II and Co I lines (peak to peak separation of .009 nm) is an example of spectral interference due to the actual physical line widths in the source.

Figure 4. ICP-FTS spectrum of Vanadium recorded at low resolution with an optical path difference of 0.98 cm. This 0.2 nm segment of the spectrum shows the V II lines at 318.851 nm (left) and 318.771 nm (right). In the unapodized case shown here, the side lobes of the spectral lines due to the instrumental sinc function are quite severe, extending to ± 20% of the peak intensity in the first cycle. The ringing side lobes are additive where they overlap due to adjacent lines.

Figure 5. ICP-FTS spectrum of Vanadium recorded at high resolution with an optical path difference of 7.06 cm. Now the observed line widths are the actual physical line widths in the source with no significant instrumental function, and an additional piece of spectral information at 318.808 nm is evident which was previously obscured by the low resolution ringing.

Figure 6. Utility of high resolution for analysis of complex spectra. Segments of the ICP-FTS spectrum of 1000 μg/ml Fe in 2000 μg/ml U matrix are shown: A. A 8 nm segment of the spectrum indicates the complexity of the emission spectrum due to the uranium matrix. Use of the Fe I line at 373.49 nm indicated by the * for quantitative analysis would not be possible at low resolution. B. An expansion of the spectrum in the vicinity of the Fe I lines shows potentially interfering weak U II lines. C. At high resolution obtained with an optical path difference of 7.06 cm, the Fe line is fully resolved from any adjacent U II lines and can be used for quantitative analysis.

Figure 7. Aliasing in a Fourier transform spectrum. A. The true spectral information. B. The positive and negative images of the spectrum generated by the FT process, symmetric about 0 on the wavenumber axis. C. The replicas or "aliases" of the spectral images, duplicated at intervals of 1/S on the wavenumber axis. D. The aliased spectrum as it will be mathematically generated by the FT process. The unaliased spectral images are indicated as black lines, and the aliased

replicas are indicated as white lines, but in the resulting spectrum there is no way to distinguish them.

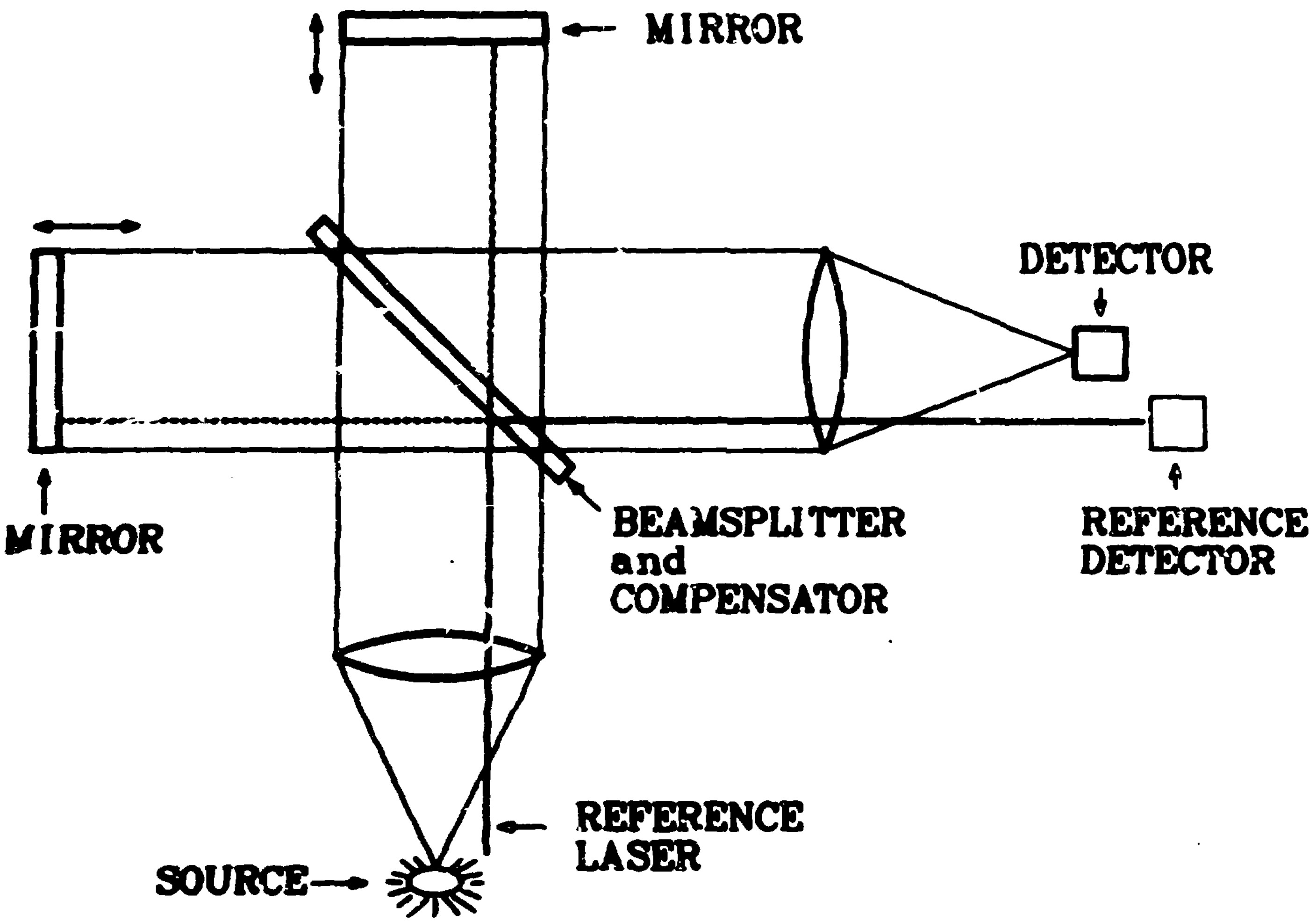

MIRROR
DETECTOR
MIRROR
BEAMSPLITTER
and
COMPENSATOR
REFERENCE
DETECTOR
REFERENCE
LASER
SOURCE

FIGURE 1

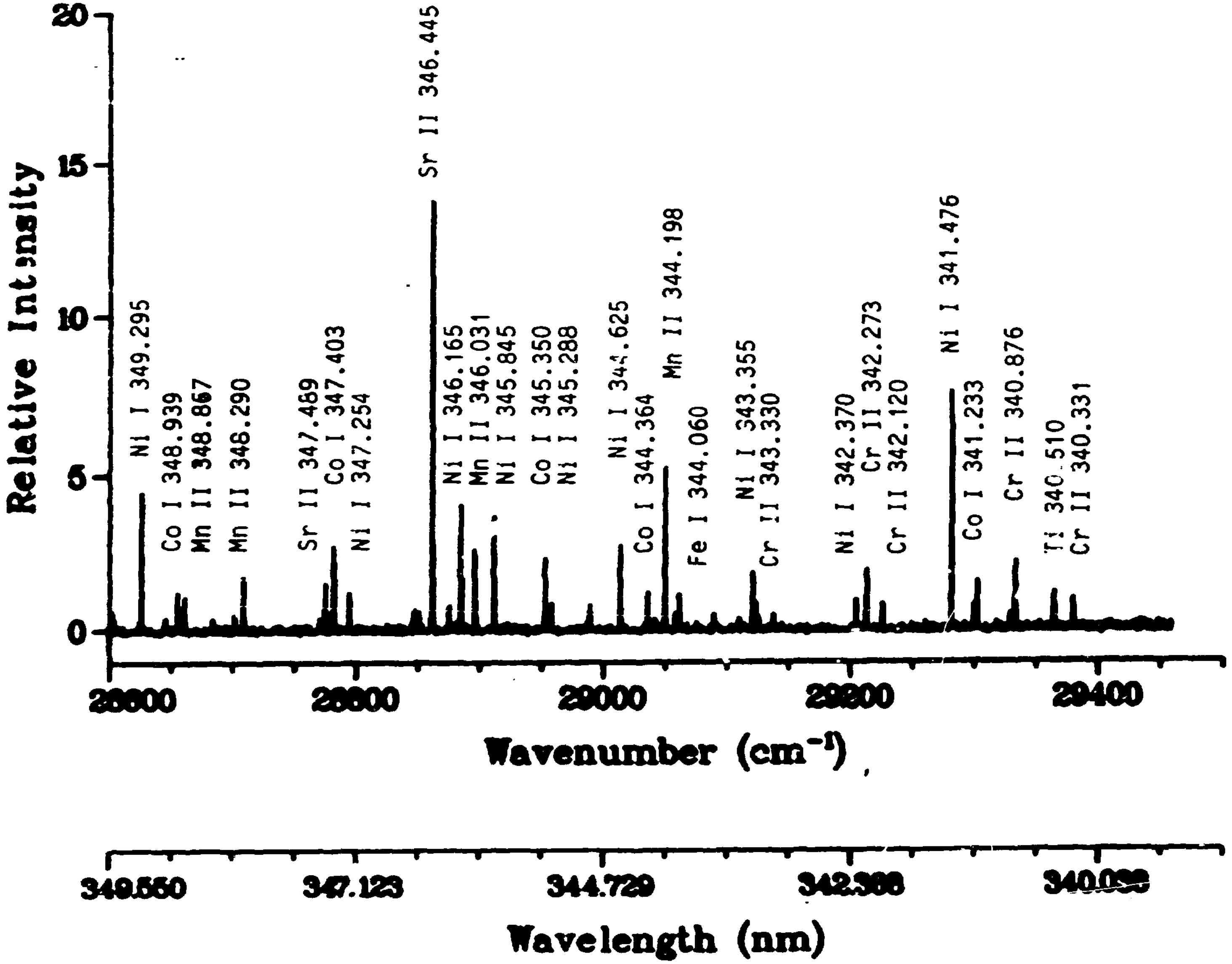

Relative Intensity
20
15
10
5
0
Ni I 349.295
Co I 348.939
Mn II 348.867
Mn II 348.290
Sr II 347.489
Co I 347.403
Ni I 347.254
Sr II 346.445
Ni I 346.165
Mn II 346.031
Ni I 345.845
Co I 345.350
Ni I 345.288
Ni I 344.625
Co I 344.364
Mn II 344.198
Fe I 344.060
Ni I 343.355
Cr II 343.330
Ni I 342.370
Cr II 342.273
Cr II 342.120
Ni I 341.476
Co I 341.233
Cr II 340.876
Ti 340.510
Cr II 340.331
28600
28800
29000
29200
29400
Wavenumber (cm⁻¹)
349.560
347.123
344.729
342.368
340.038
Wavelength (nm)

FIGURE 2

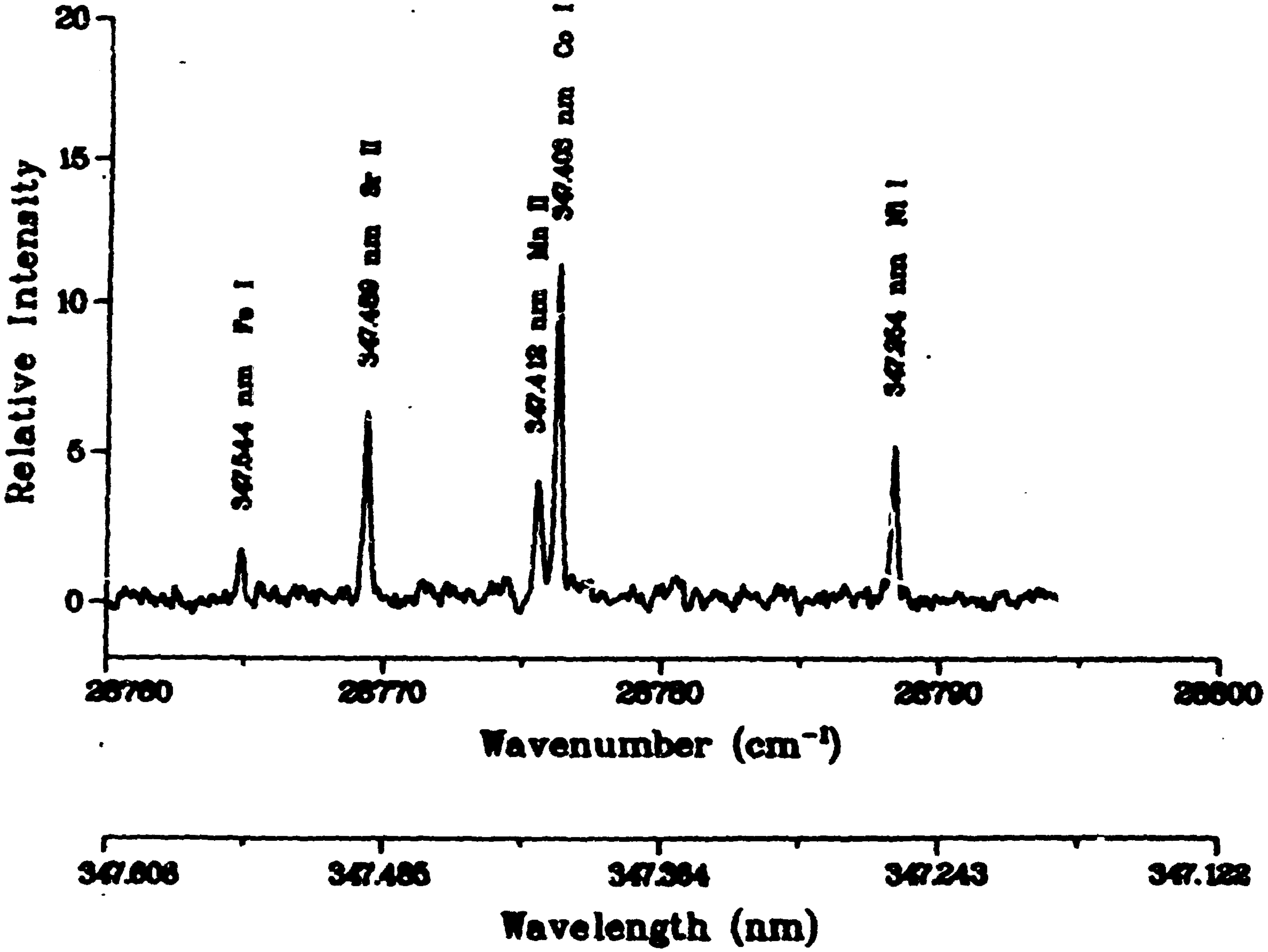

347.544 nm Fe I
347.489 nm Sr II
347.412 nm Mn II
347.403 nm Co I
347.264 nm Ni I
Relative Intensity
20
15
10
5
0
28760
28770
28780
28790
28800
Wavenumber (cm⁻¹)
347.608
347.485
347.364
347.243
347.122
Wavelength (nm)

FIGURE 3

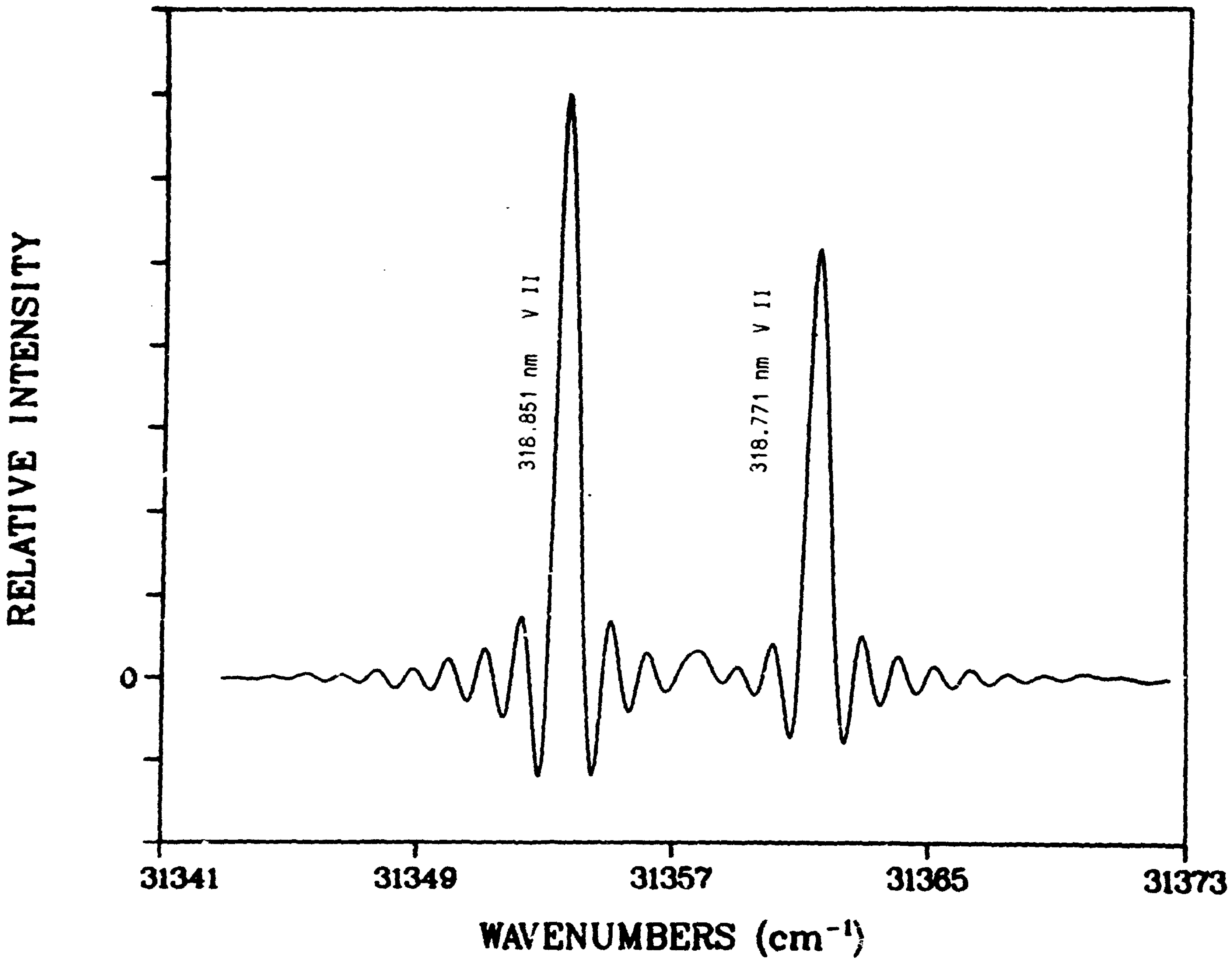

RELATIVE INTENSITY
0
318.851 nm V II
318.771 nm V II
31341
31349
31357
31365
31373
WAVENUMBERS (cm$^{-1}$)

FIGURE 4

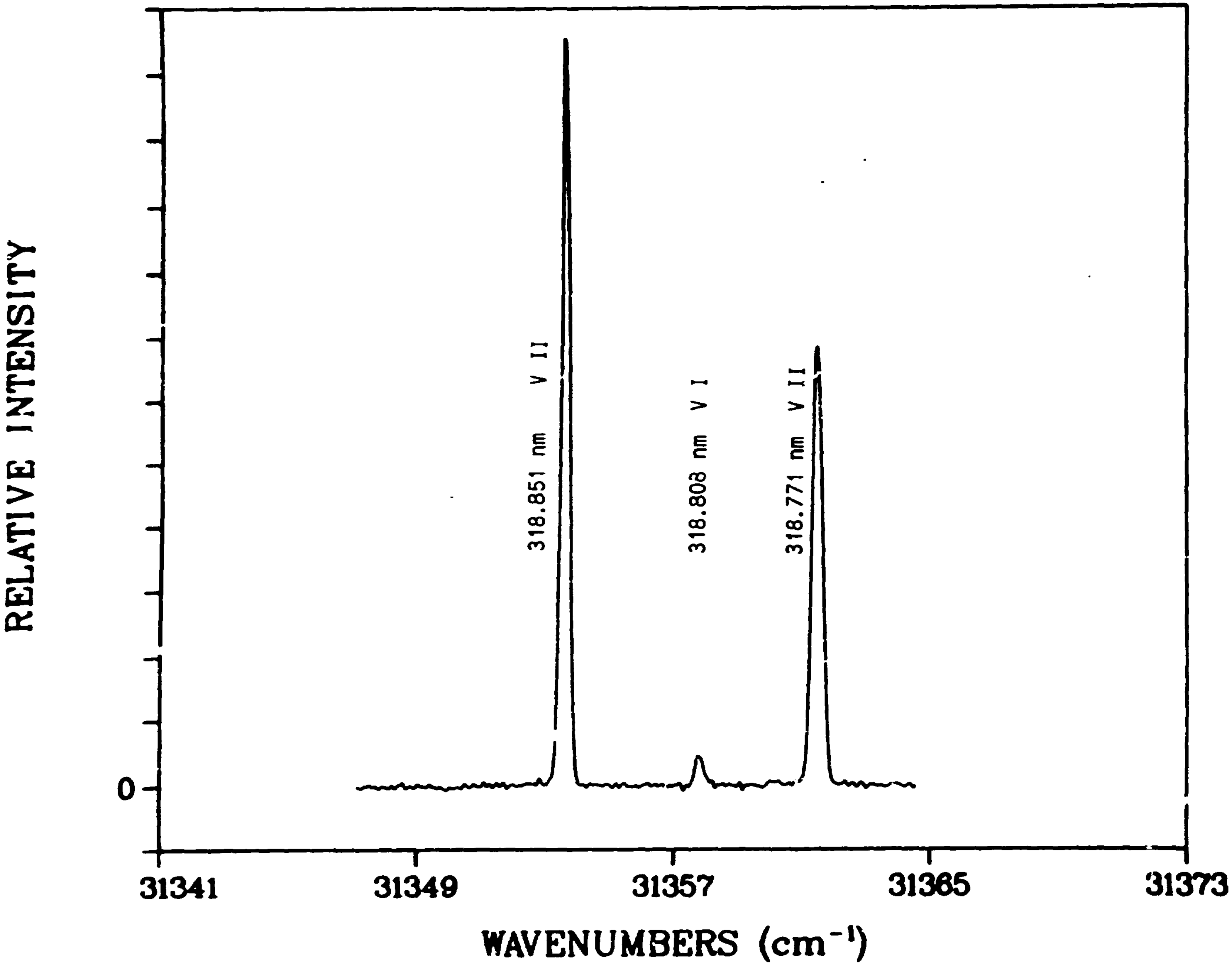
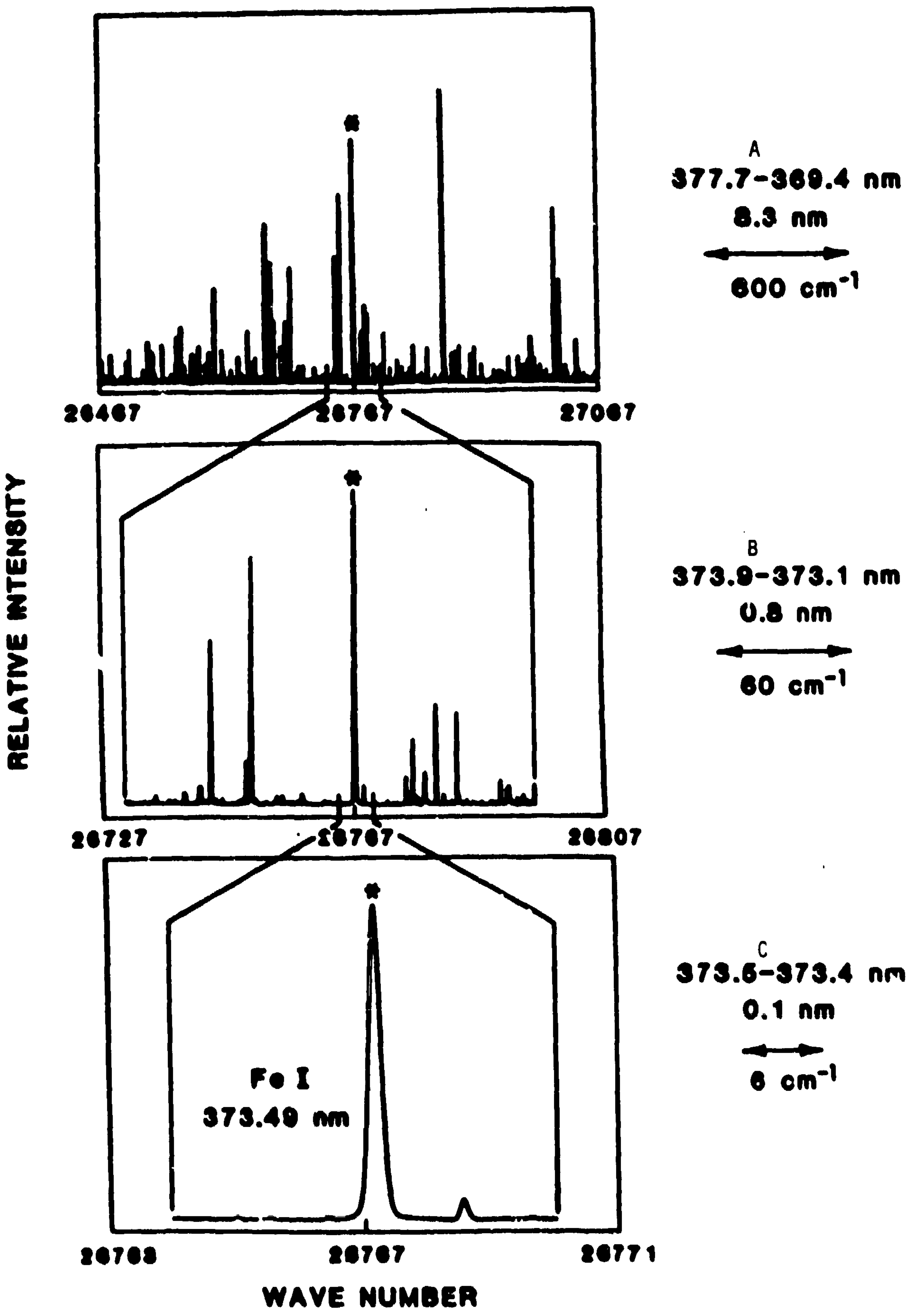

RELATIVE INTENSITY
0
318.851 nm V II
318.808 nm V I
318.771 nm V II
31341
31349
31357
31365
31373
WAVENUMBERS (cm⁻¹)

FIGURE 5

FIGURE 6



*
26467
26767
27067
A
377.7-369.4 nm
8.3 nm
600 cm$^{-1}$
*
26727
26767
26807
B
373.9-373.1 nm
0.8 nm
60 cm$^{-1}$
*
Fe I
373.49 nm
26763
26767
26771
C
373.5-373.4 nm
0.1 nm
6 cm$^{-1}$
RELATIVE INTENSITY
WAVE NUMBER

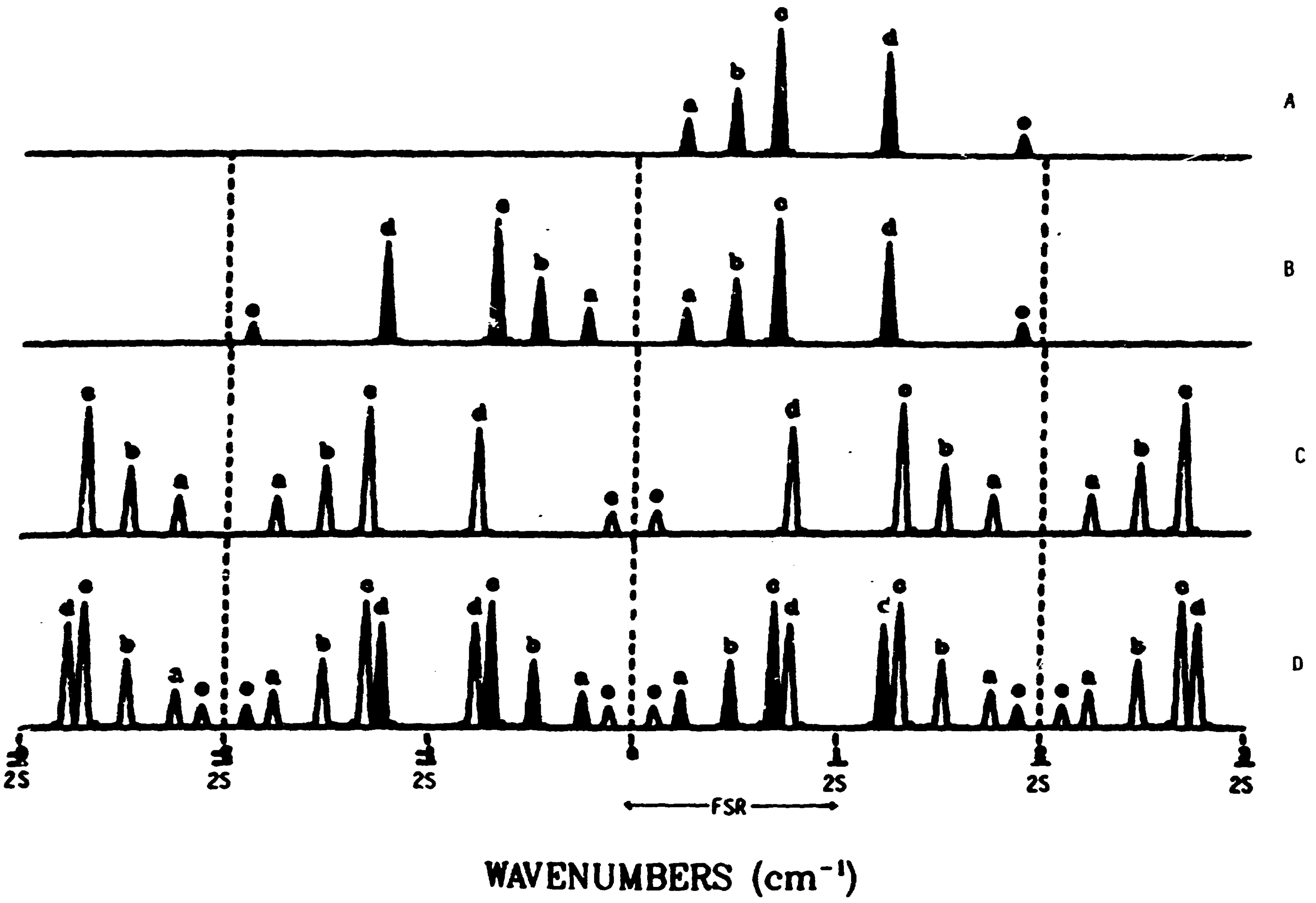


FIGURE 7