Coal Liquefaction Process Streams Characterization and Evaluation

UV Resonance Raman Studies of Coal Liquid Residuals

Topical Report
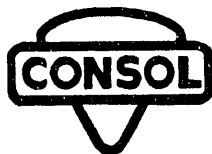
Prepared by:

University of Pittsburgh
Department of Chemistry
Pittsburgh, PA 15260

Sanford A. Asher

Prepared for:

CONSOL Inc.
Research & Development
4000 Brownsville Road
Library, PA 15129

F. P. Burke
R. A. Winschel
S. D. Brandes

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Under Contract to:

PROJECT ASSESSMENT

Introduction

Under subcontract from CONSOL Inc. (U.S. DOE Contract No. DE-AC22-89PC89883), the University of Pittsburgh studied the use of ultraviolet resonance Raman (UVRR) spectroscopy for the characterization of coal liquefaction resids. The full report authored by the University of Pittsburgh researchers is presented here. The following assessment briefly highlights the major findings of the project, and evaluates the potential of the method for application to coal-derived materials. These results will be incorporated by CONSOL into a general overview of the application of novel analytical techniques to coal-derived materials at the conclusion of this contract.

Summary

This study suggests that with further development the UVRR spectroscopy method may prove useful for the examination of the aromatic and unsaturated species in distillation resid materials derived from direct coal liquefaction. The technique, which was previously used for the examination of polycyclic aromatic hydrocarbons (PAH) in bio-medical materials, petroleum, and polymer systems, was applied to the tetrahydrofuran (THF)-soluble portion of six 850°F⁺ distillation resids. The results of this study indicate that the UVRR method may, with additional development, become a useful tool for the analysis of the PAHs in coal-derived materials.

Program Description

This report describes the work performed at the University of Pittsburgh under a subcontract from CONSOL Inc., Research and Development. CONSOL's prime contract to the U.S. Department of Energy (Contract No. DE-AC22-89PC89883, "Coal Liquefaction Process Streams Characterization and Evaluation") established a program for the analysis of direct coal liquefaction derived materials. The program involves a number of participating organizations whose analytical expertise is being applied to these materials. This Participants Program has two main objectives. The broad objective is to improve our understanding of fundamental coal liquefaction chemistry to facilitate process improvement and new process

development. The specific approach to achieving this objective is to provide a bridge between direct coal liquefaction process development and analytical chemistry by demonstrating the application of various advanced analytical methods to coal liquefaction materials. The methodologies (or techniques) of interest are those which are novel in their application for the support of coal liquefaction and those which have not been fully demonstrated in this application. CONSOL is providing well-documented samples from different direct coal liquefaction production facilities to the program participants. The participants are required to interpret their analytical data in context to the processing conditions under which the samples were generated. The methodology employed is then evaluated for its usefulness in analyzing direct coal liquefaction derived materials.

Participant's Methodology

The University of Pittsburgh used UV resonance Raman spectroscopy with a continuous wave (CW) laser source for the examination of the tetrahydrofuran (THF)-soluble portion of six $850°F^+$ distillation resids. The samples were produced at the Wilsonville pilot plant. Samples were taken from two locations: between the reactors, and after the second-stage reactor. These samples are expected to represent different extents of coal liquefaction. The samples are composites of samples taken over long periods of individual processing runs. Two major processing parameters were varied among the Wilsonville runs: feed coal and reactor configuration (thermal/catalytic vs catalytic/catalytic). The UVRR experiments utilizing the CW UV laser are described on pages 8 through 9 of the attached report.

Participant's Major Findings

The following principal observations for the application of UVRR spectroscopy to coal liquefaction materials were reported by the University of Pittsburgh. An expanded discussion can be found in the attached report, pages 10 through 13.

The THF-soluble samples were resolubilized in THF and examined. These same samples were extracted with acetonitrile and examined as solutions. The acetonitrile-extraction residues were solubilized in THF and also

examined. It was found that the Raman spectrum of the material extracted into the acetonitrile fraction was different than that of the whole samples and contains species that absorb less strongly than the original samples. It was possible to distinguish differences in the spectra of the THF-soluble and acetonitrile-soluble portion of each sample. In addition, the acetonitrile-extraction residues (resolubilized in THF) have a larger bandwidth for the 1630 cm^{-1} peak and the shoulder at 1560 cm^{-1} is absent. This is especially true for the Run 257 second-stage product, the Run 260 second-stage product, and the Run 261 interstage sample. There was, however, little sample-to-sample difference evident among the THF-soluble or acetonitrile-soluble portions of the samples. The broad peaks evident in all the spectra indicate that numerous species are adsorbing in the same region.

In this study it was found that the solid resid samples could be examined without solubilization. It was found, however, that the solid samples must be spun under the laser light to prevent localized heating. Further study with the solid samples was not pursued under this contract.

CONSOL Evaluation

In this study, a brief exploration of the UVRR spectroscopy technique was made with direct coal liquefaction-derived materials. It was found that the materials can be examined in the solid state; however, the parameters of measurement were not fully explored in this study. Neither identification and quantification of the species present in the samples, nor speciation by aromatic ring conjugation was accomplished. Higher resolution spectra would be required to accomplish either. In addition, a complete library of reference spectra constructed with model compounds would be required to thoroughly complete this task. It is believed that the ease of examining samples as solids will be advantageous for future work.

The Raman spectrometer used in these studies costs on the order of $200,000. It is not, presently, commercially available equipment. The time required to produce a single spectrum is about five minutes.

Further Development

The UVRR spectroscopy technique was explored in this project. A number of avenues for further research are suggested based on the major findings presented here. 1) It was found that solid coal-derived resid materials can be examined by the UVRR technique without solubilization. This would be the preferred method to use in any future work with resids. 2) The use of the next generation of instrumentation, which is becoming commercially available and has higher resolution, would be advantageous in determining the species present in the coal-derived materials. The author recommends the following techniques to obtain higher resolution with the present instrumentation 1) "Raman hole burning", 2) "saturation" techniques and 3) collection of spectra at low temperature. Additionally, the author specifies the need to assemble a reference library of Raman spectra from suitable model compounds before molecular speciation can be routinely accomplished with complex mixtures such as coal-derived resids.

Participant's Statement of Work

UV Resonance Raman Spectroscopy (UVRRS) is a technique which has been used for the investigation of bio-medical materials, petroleum, and polymers. It also has been used to examine several coal-derived liquids. It has not, however, been demonstrated for its ability to answer questions pertaining to the chemistry of coal conversion. The UVRRS technique has the potential to speciate and quantify the various conjugated aromatic ring structures in coal liquids. This information, not readily obtainable by other routes, should be of value for understanding factors affecting resid properties and reactivity. As such, it fits well within the scope of the participants program.

The application of UVRRS to a set of six samples will allow a demonstration of the value of this technique for the examination, speciation, and quantitation of the polyaromatic hydrocarbon structures in coal liquefaction-derived resids. These samples have been selected (see attached list) so that the utility of UVRRS for characterizing liquefaction resids can be evaluated. The samples will be supplied to the University of Pittsburgh with the following information, as available: elemental analyses, ash content, ash elemental analysis, phenolic OH

concentration, calorific value, hydrogen classes by ^{1}H-NMR, and the full history of the sample (plant, process conditions, age, and storage conditions). The six samples are tetrahydrofuran (THF)-soluble, non-distillable residual materials. Sample size will be at least 10g. The samples will be brittle pitch-like materials that will be supplied as approximately minus 60 mesh powder.

The samples will be solubilized in a good solvent for coal liquids (THF or pyridine), cast as a film on a support which can be moved past the focal point of the laser to prevent localized heating, then analyzed by the UVRRS technique. The six samples will be characterized by groups of differing ring conjugation (separately 2, 3, and 4 conjugated-ring groups, and possibly 5 and 6 conjugated-ring groups). Speciation of compounds within these groups also will be attempted.

UV RESONANCE RAMAN STUDIES OF COAL LIQUID RESIDUALS

Sanford A. Asher
Department of Chemistry
University of Pittsburgh
Pittsburgh, PA 15260
FAX 412-624-0588
412-624-8570

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EXECUTIVE SUMMARY

We demonstrated the utility of UV resonance Raman spectroscopy to study aromatic and unsaturated species in coal liquid residuals. The samples examined were obtained from different coal liquefaction runs utilizing different coals. Some of the differences involved either two stages of catalytic hydrogenation or only one stage.

UV resonance Raman spectroscopy is a new technique which is being developed for uses in analytical chemistry and biochemistry as well as for fundamental physical chemical studies. It involves exciting samples with UV light and examining the frequencies and intensities of the Raman scattered light. Polycyclic aromatic hydrocarbons (PAH) are intense UV Raman scatters. We have demonstrated that it is easy to study them at low concentrations and in complex environments. Previous studies demonstrated we could monitor PAH in coal derived liquids. In this study we examined coal residuals.

We utilized a new continuous wave (CW) laser source which we demonstrated had important advantages for these types of studies. We demonstrated that we could examine the solid residuals using this laser, and that the only requirement is that we must spin the sample to distribute the sample heating. We also examined the residuals dissolved in tetrahydrofuran (THF), a solvent in which they are completely soluble. We also extracted the residuals with acetonitrile and compared the Raman spectra of the acetonitrile solubles, to the complete residuals in THF solution and the acetonitrile extracted solid residual dissolved in THF. We see differences between the spectra of the different samples.

Although we detect differences, we do not have sufficient information to correlate the spectral differences to particular components. UV resonance Raman spectroscopy is a new technique which does not as yet have a large library of spectra. The incisive use of this technique for these kinds of studies will require measuring extracts of the residuals and the creation of a library of reference compounds.

INTRODUCTION

UV resonance Raman spectroscopy (UVRR)[1] offers high selectivity and sensitivity for studying the vibrational spectra of the great majority of all molecules which have electronic absorption bands at wavelengths longer than 180 nm. This includes essentially all organics with at least one double bond and also includes most inorganic compounds. Excitation into the UV absorption bands of polycyclic aromatic hydrocarbons (PAH's) such as pyrene,[2] for example, enhances the Raman cross section by factors of 10^8, which permits studies of low concentrations of these analytes in complex environments.[3-6] The recent development of instrumentation[7,8] capable of UV excitation in the region between 180 nm and 300 nm now permits the study of aromatic amino acids in proteins,[9-14] and DNA nucleic acid structural studies.[15] UVRR has also been used to examine the nature of molecular electronic excited states of small molecules;[16-18] for example, UVRR studies of amides have indicated that the amide π^* excited state is twisted.[19-21] The high selectivity and sensitivity of this technique permits important analytical applications. Examples include studies of PAH's in coal derived liquids[4-6] and in petroleum fractions,[22] as well the use of UVRR for examining low levels of unsaturation in polymers.[22,23] The utility of UVRR results not only from the resonance enhancement phenomenon, but also because fluorescence interference within the Raman spectrum does not occur in condensed phase samples excited below 250 nm;[24] fluorescence interference from impurities is a major impediment for Raman studies utilizing near UV, visible or near IR excitation.

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The strong resonance enhancement which occurs with UV Raman excitation permits spectral measurements with high signal-to noise ratios (S/N); however, the typical S/N ratios remain far below the theoretical limit, mainly because of the optical excitation sampling limitations which result from the typical high pulse energy flux laser excitation generally used. Until now, UV Raman measurements have utilized frequency doubled YAG or XeCl excimer lasers[7,13,16] with pulse widths of ca 10 nsec and repetition rates lower than 300 Hz. These lasers pump near UV or visible wavelength dye lasers. The pulsed dye laser outputs which have very high peak powers are converted into the UV through nonlinear optical processes, such as nonlinear frequency doubling and frequency mixing. The result is completely tunable UV light at relatively low duty cycles with very high peak powers. The laser outputs easily obtained have average powers of tens of milliWatts with peak powers of many megaWatts. Focused these pulses easily cause dielectric breakdown in any sample. Other nonlinear optical phenomena occur even with more diffuse focusing and lower peak powers to compete with the Raman scattering[25]. At even lower peak powers Raman saturation phenomena can occur which depopulates the ground state and creates transient concentrations of excited state species.[10,19a,25,26] To avoid saturation and nonlinear phenomena pulsed Raman measurements should be obtained with broad defocused laser beams with pulse energy flux densities of less than 1 mJ/cm^2.

The Raman spectrometers used for these measurements require high resolution and utilize narrow slits, generally of 100 to 200 μm width. Given the large f/number required for the spectrograph stage, only a small portion of the illuminated sample width can be

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focused into the spectrometer. In order to have an incident energy flux density of less than 1 mJ/cm^2, with an incident average power of 20 mW, less than 1% of the incident laser photons can be utilized in a typical backscattering collection geometry, that utilizes a collection optic with a magnification of six, a detector of 2.5 mm height and a slitwidth of 200 μm in Raman measurements utilizing the 20 Hz repetition rate YAG laser system. Less than 10% can be utilized for the 200 Hz excimer laser for samples such as pyrene[2] and tryptophan[25] which have significant excited state lifetimes, and which are susceptible to ground state depletion.

The advent of the high repetition rate excimer laser has increased the spectral S/N ratios for resonance Raman measurements; however, the increased maintenance and low laser dye lifetimes makes it an expensive laser in cost and reliability.[27] Beneficially, however, the excimer laser has permitted UV Raman studies of species with significant excited state lifetimes such as tryptophan.[12a] Most recently other groups[22,28] have developed quasi-CW UV sources that employ mode locked YAG Lasers which give extremely high repetition rates and are considered quasi-CW since they have a duty cycles of almost 0.01, which are much higher than that of the highest repetition rate excimer laser system (500 Hz) which has a duty cycle of less than 10^{-5}. These systems give good S/N spectra, but are relatively expensive and complex, as are the YAG and excimer systems typically used. In this study we utilize a new CW UV laser which dramatically improves the spectral S/N and permits new applications of UV resonance Raman in analytical chemistry.

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EXPERIMENTAL

This report here describes a new CW UV laser based on an intracavity frequency doubled Ar^+ ion laser which has output wavelengths and powers shown in Table I. There are five frequency doubled lines below 260 nm which are obtained by frequency doubling the strong Ar^+ ion lasing lines in the visible spectral region. The laser is constructed around a small frame Coherent Inc. Innova 300 Ar^+ ion laser system. The output coupler is removed and a modified optical cavity is constructed in which the intracavity beam waist is focused at the center of a BBO doubling crystal. A dielectric mirror, which is completely reflective in the visible but transmittive in the UV is used as the output coupler. We convert the elliptical output beam to a circular beam by use of a cylindrical lens. To maximize the frequency doubled beam intensity stability and its pointing stability, the temperature of the BBO crystal is thermostatically controlled at a temperature slightly elevated over ambient. In addition, a small portion of the UV beam is split off and monitored by a photocell which maximizes the UV output power by controlling both a signal to the Ar^+ ion laser power supply feedback loop which controls the plasma tube current, and by controlling a signal which keeps the laser cavity mirror optimally aligned by use of a servo controlled actively stabilized optical cavity. The laser output also contains plasma emission lines and the UV output is dispersed by a Pellin Broca prism over a long (ca 2 m) pathlength in order to separate and remove the plasma emission lines. It is essential to use a fused silica Pellin Broca prism rather than a crystalline quartz prism to disperse the nonpolarized plasma lines;

the birefringent crystalline quartz will overlap the dispersions of the two polarizations and make it difficult to isolate the lasing line.

The frequency doubled Ar^+ ion laser requires careful alignment of the doubling optics when tuning between different UV lines, but once tuned and aligned it is indefinitely stable. We expect that the lifetime of the BBO crystals is finite and that they will need to be replaced at regular intervals. We see some damage in the BBO crystals when operated over extended periods of time at the highest powers. However it appears that we will obtain hundreds of hours of use at the typical powers we are likely to use for spectral measurements. The samples studied are listed in Table II.

RESULTS

Figure 1 shows the absorption spectra of the six residual samples dissolved in tetrahydrofuran (THF), while Figure 2 shows the absorption spectra of the same samples first extracted with acetonitrile (AC) and then dissolved in THF. Sample concentrations were 0.2 gm/L and the pathlength was 0.2 cm. The figures also show the absorption spectrum of the pure THF solvent. The absorption below 210 nm results from aromatic unsaturated species in the sample. The differences in the spectra indicate differences in composition. The broad features and shoulders hint of particular species present in the solution. The acetonitrile extracted resids show absorption spectra that differ from the original resids. The fact that the average absorptivity increases indicates that the acetonitrile selectively extracts species which absorb less than that of the original resid sample.

Figures 3A-F show the 228.9 nm excited UV Raman spectra of the original resid samples dissolved in THF, spectra of the acetonitrile extracts and spectra of the acetonitrile extracted residuals in THF. The top spectrum is of the original sample dissolved in THF. The middle spectrum is the AC extract, while the bottom spectrum is of the AC extracted solid resid dissolved in THF. In all cases, the spectra have had the solvent bands removed by numerical subtraction of Raman spectra of the pure solvent. The Raman spectra of the original resid samples are similar, and show a broad peak at $\underline{ca}$ 1630 cm^{-1} and a weak shoulder at $\underline{ca}$ 1560 cm^{-1} and some evidence of a peak around 1400 cm^{-1}. Previous UV Raman studies of PAH such as naphthalene and pyrene as well as conjugated unsaturated species such as carotenes indicate that these types of compounds often show intense features

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in this entire spectral region. These bands derive from C=C stretching vibrations. The position of the 1630 cm^{-1} band is essentially identical between samples except for sample 4 where the peak is slightly narrower and shifted a few cm^{-1} to higher frequency compared to the average of the samples.

The spectra of that portion of the resids which are soluble in AC shows a narrower peak at ca 1630 cm^{-1} which is shifted to somewhat higher frequency than either that from the entire sample, or that portion redissolved in THF which was not soluble in AC. The narrowed peak indicates a smaller number of constituents. Samples 1, 2 and 5B show a relatively large shift of ca 17 cm^{-1} whereas the remaining samples show a smaller shift of a few cm^{-1}.

The remaining resid samples extracted by AC and dissolved in THF all show similar peaks at 1630 cm^{-1}. In addition, except for sample 5A, a strong peak occurs at ca 1380 cm^{-1} in these samples. All of the samples, with the exception of sample 5A, show a weaker peak at 1470 cm^{-1}, whose intensity differs between spectra. Sample 5A uniquely shows no evidence of this band.

Figures 4A-F shows spectra excited at 244 nm. These spectra show a much narrower peak at ca 1640 cm^{-1} and the presence of a shoulder at 1560 cm^{-1}. In addition, a very broad peak at 1400 cm^{-1} occurs. The AC extracted spectra are quite similar, but the peak is shifted ca 5 cm^{-1} to lower frequency. In addition, the broad peak at 1400 cm^{-1} appears narrower, and the shoulder at 1560 cm^{-1} is more evident.

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The THF solutions of the extracted resid are much broader and the 1560 cm^{-1} shoulder is gone, in most cases. The different samples show clear bandwidth differences for the AC extracted resids dissolved in THF. Samples 2, 4 and 5B have a larger bandwidth than the other samples.

Figures 5A, B, C and D show 244 nm excited difference spectra of samples 1, 2, 5A and 5B. Figure 5A also shows the difference spectrum obtained with 228.9 nm excitation. The difference spectra were obtained by subtracting the spectrum of the acetonitrile extracted resid, which was dissolved in THF, from the THF solution of the original resid sample. At 244 nm we observe a narrow peak at ca 1630 cm^{-1} for all of the samples as well as weaker peaks at 1560 cm^{-1} and 1415 cm^{-1}. These peaks derive from the species which were extracted by the acetonitrile. The fact that these difference spectral features differ from the acetonitrile solution spectra indicate that some chemical alterations may be occurring in the samples due to acetonitrile extraction. This is a surprising result and which will require further work if it is to be understood. The 228.9 nm difference spectra for Sample 1 is quite different from the 244 nm difference spectrum. This is consistent with the fact that different species are observed with the 228.9 nm excitation, as expected.

Figure 6 shows the ability of the CW Ar^{+} ion laser source to obtain resonance Raman spectra of solid samples. Figure 6 compares spectra of sample #2 of the coal liquid resids. Figures 6A and 6B spectra are of a stationary and spinning solid film prepared by drying a tetrahydrofuran solution of the residuals on an aluminum block. All of the spectra show a dominating peak between 1620-1640 cm^{-1}. The Figure 5A stationary spectrum shows a

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broadened peak around 1620 cm^{-1} which is shifted to lower frequency compared to the spinning sample (Fig. 5B). We believe this broadening and shifting results from sample heating, or formation of long lived excited species. Spinning the sample in the beam distributes the laser energy and the spectrum closely resembles that of the same sample dissolved in tetrahydrofuran, in which it is completely soluble (Fig. 5C). Essentially identical spectra can be obtained from the resids by packing the powder into a quartz capillary. All of the 244 nm excited spectra show the dominating presence of a band at ca 1630 cm^{-1} and broader features between 1300-1400 cm^{-1}, which result from ring breathing motions of polycyclic aromatic hydrocarbon rings[2-6]. We are in the process of determining the species present in the coal liquid residuals. The importance of these data shown here is the fact that the CW laser makes it possible, for the first time, to study the UV Raman spectra of solid absorbing samples. The steady state temperature rise which occurs with the CW laser is much less than with the pulsed laser; if the sample is spun, the temperature rise is negligible (< 1 K), and the samples do not thermally decompose. Thus, solid samples can be studied as packed powders with essentially no sample preparation.

We conclude small spectral differences can be observed between samples and that these differences are from different compositions. The different excitation wavelengths selectively monitor different species.

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RECOMMENDATIONS

We have demonstrated that UV Raman can detect differences between samples. More careful measurements are required to quantitate these differences and to relate them to particular species. Higher resolution spectra would be an invaluable aid. We can either repeat these studies at low temperatures or utilize Raman hole burning and saturation techniques to increase the resolution. These techniques increase selectivity by spectrally removing species from the sample by selectively exciting them with a second laser source. It is essential to construct a library of reference compounds in order to relate the spectral features to molecular species.

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TABLE I. CW Ar$^+$ ion laser wavelengths and output powers.

Wavelength (nm)	Power (mW)
228.9	30
238.3	100
244.0	400
248.3	180
257.3	750
275.4	5
300-305.5	20
333.4	40
333.8	30
335.8	20
351.1	200
351.4	60
363.8	240
454.5	140
457.9	420
465.8	180
472.7	240
476.5	720
488.0	1800
496.5	720
501.7	480
514.5	2400
528.7	420

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TABLE II.

SAMPLES

Ref. No.	Coal Feed	Source/Conditions	Comments
1	Illinois No. 6	W; Run 250; T/C	Interstage
2	Illinois No. 6	W; Run 257; C/C	Second Statge Product
3	Pittsburgh No. 8	W; Run 259; C/C	Interstage
4	Wyodak and Anderson	W; Run 260; C/T	Second Stage Product
5A	Wyodak and Anderson	W; Run 262; C/C	Interstage
5B	Illinois No. 6	W; Run 261; C/C	Interstage

Note: Samples are THF-soluble distillation resids; C/C = Catalytic/Catalytic; T/C = Thermal/Catalytic; W = Wilsonville
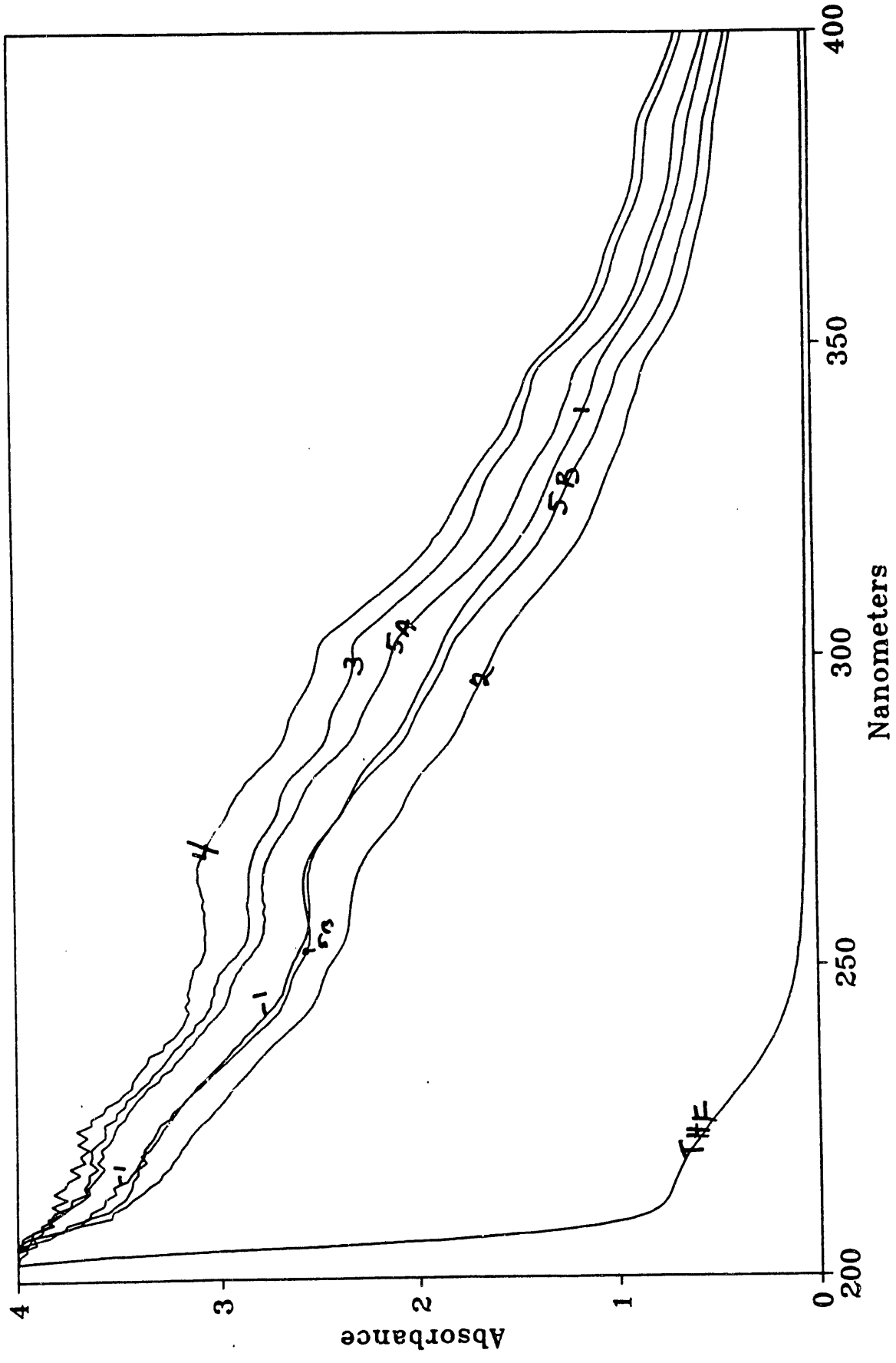
81THF1   Res= 1

L10-81-1 neat; 2mm

11/10/92 12:57

Figure 1

0.25
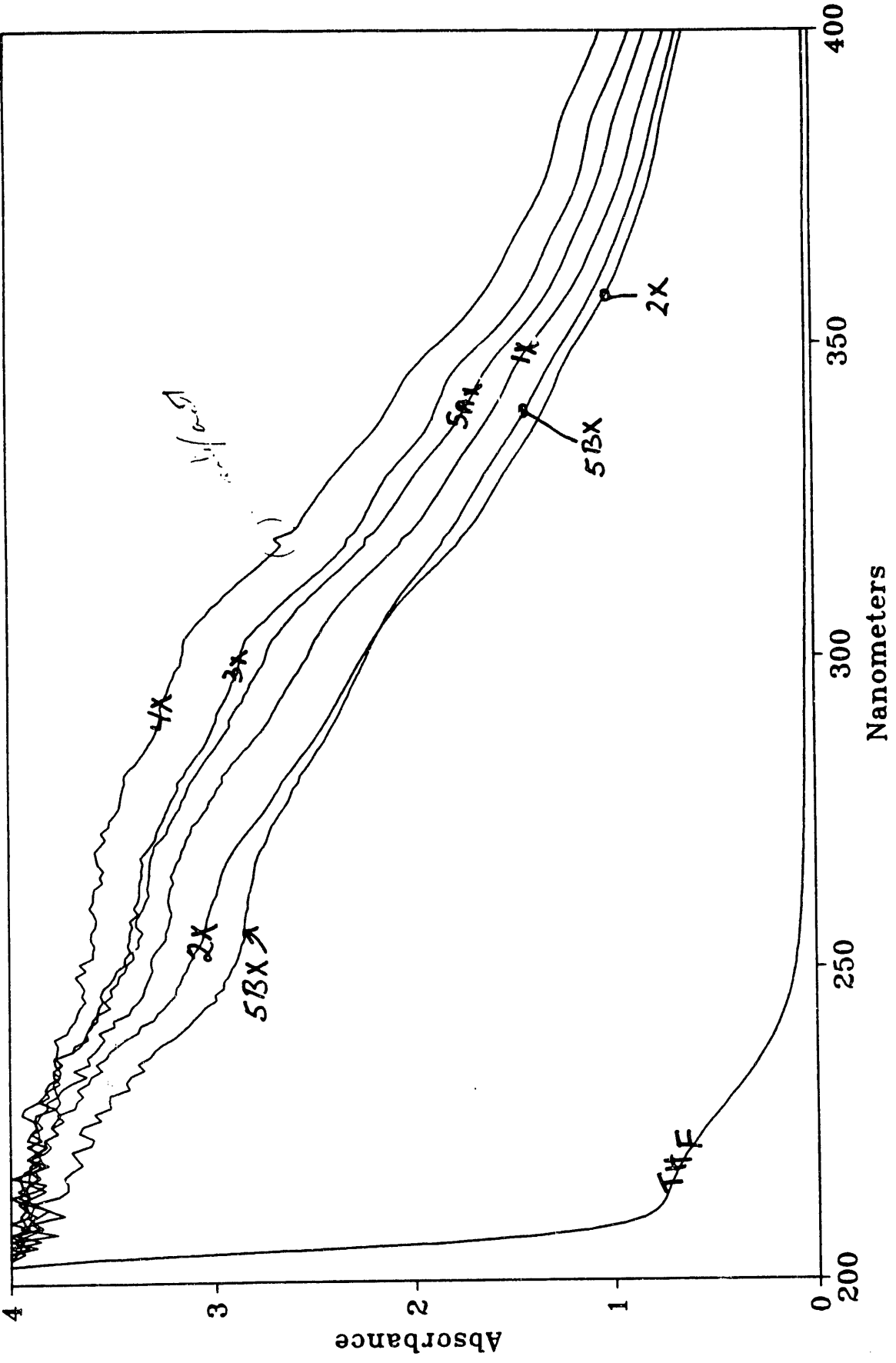
84XTHF6   Res=   1

L10-84-5BX neat; 2mm.   5 Nov 92.

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Figure 2

22
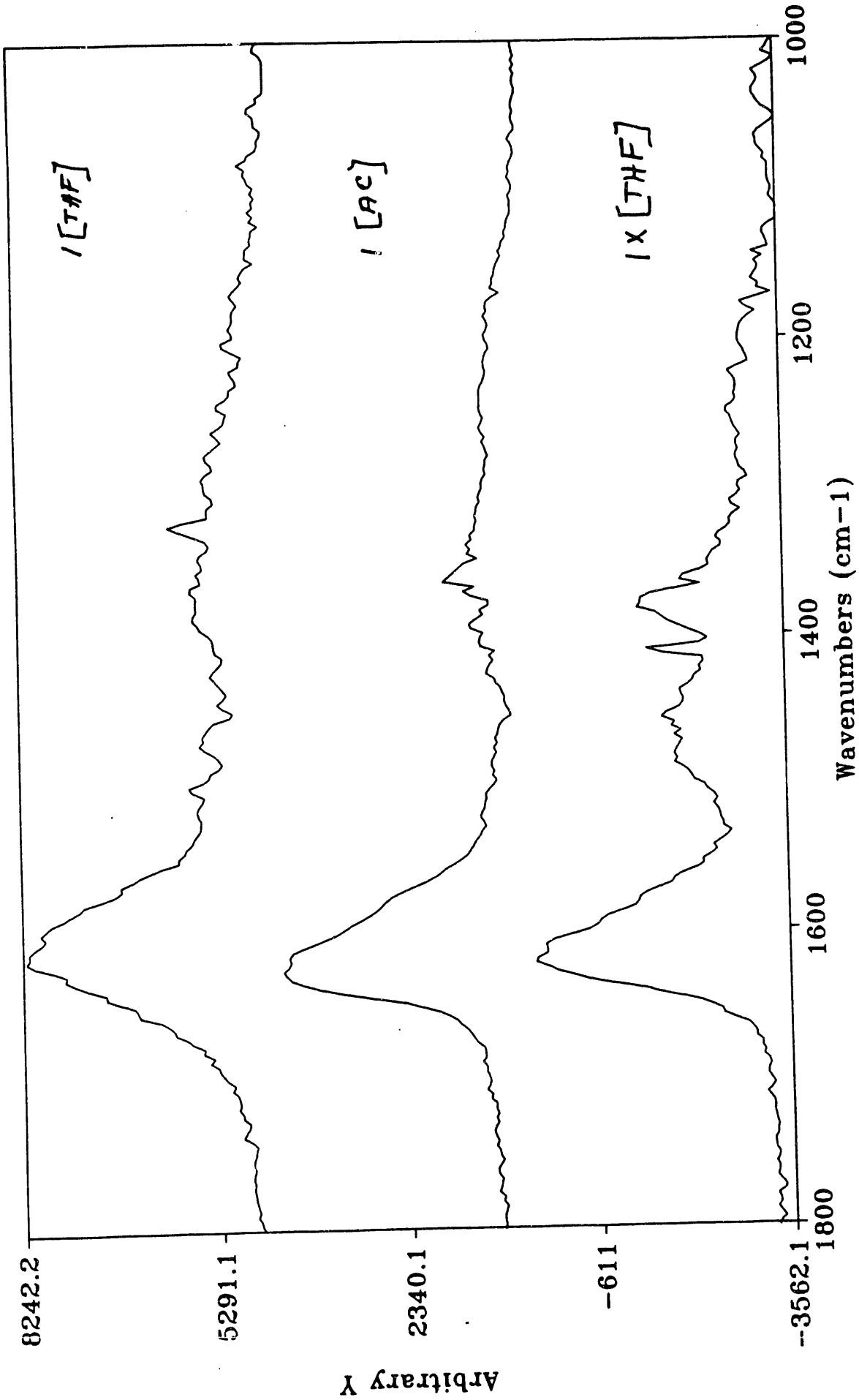
Res= 1

Figure 3A. Sample #1

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Wavenumbers (cm−1)

Arbitrary Y

D73S2D71F

491490

23
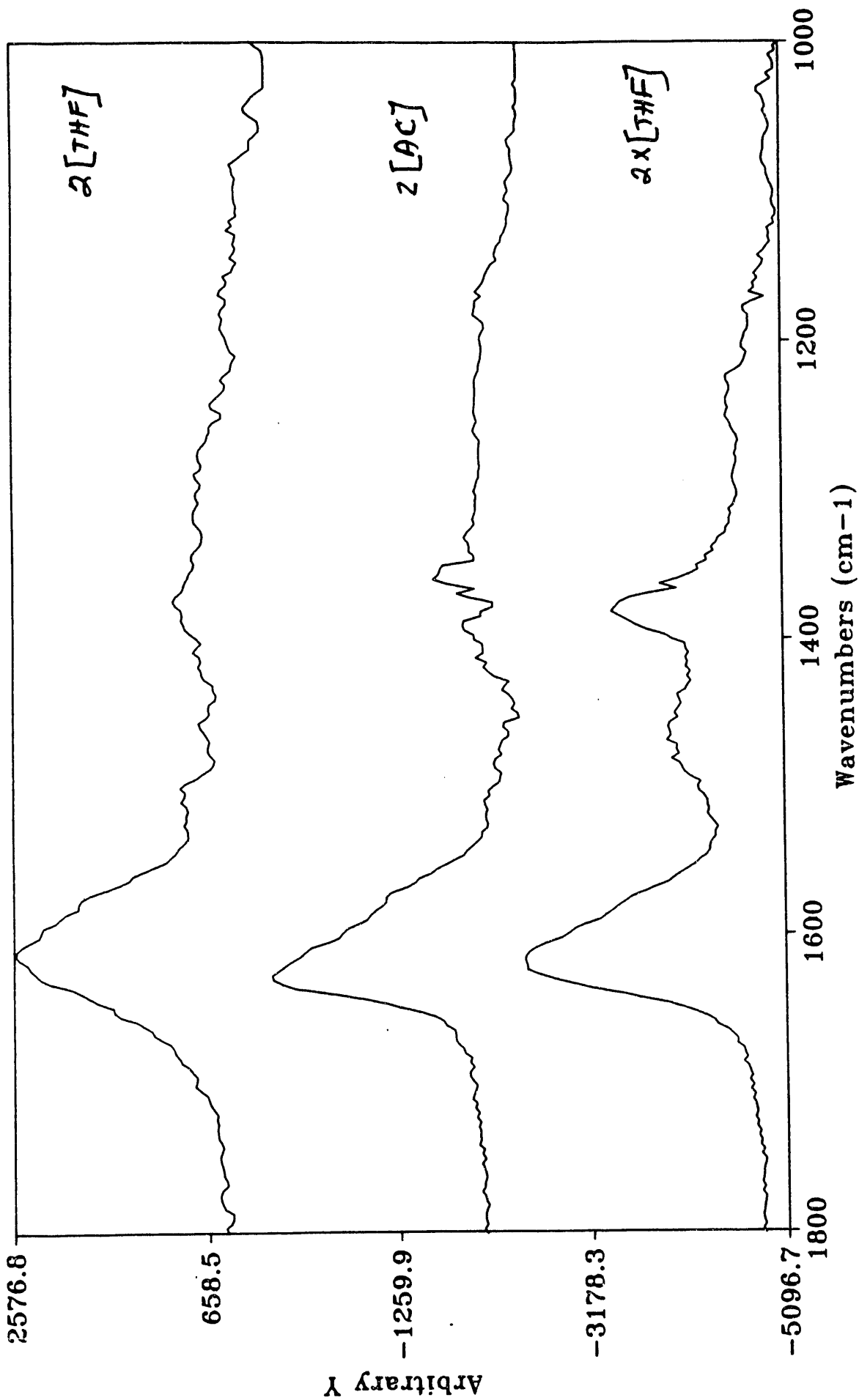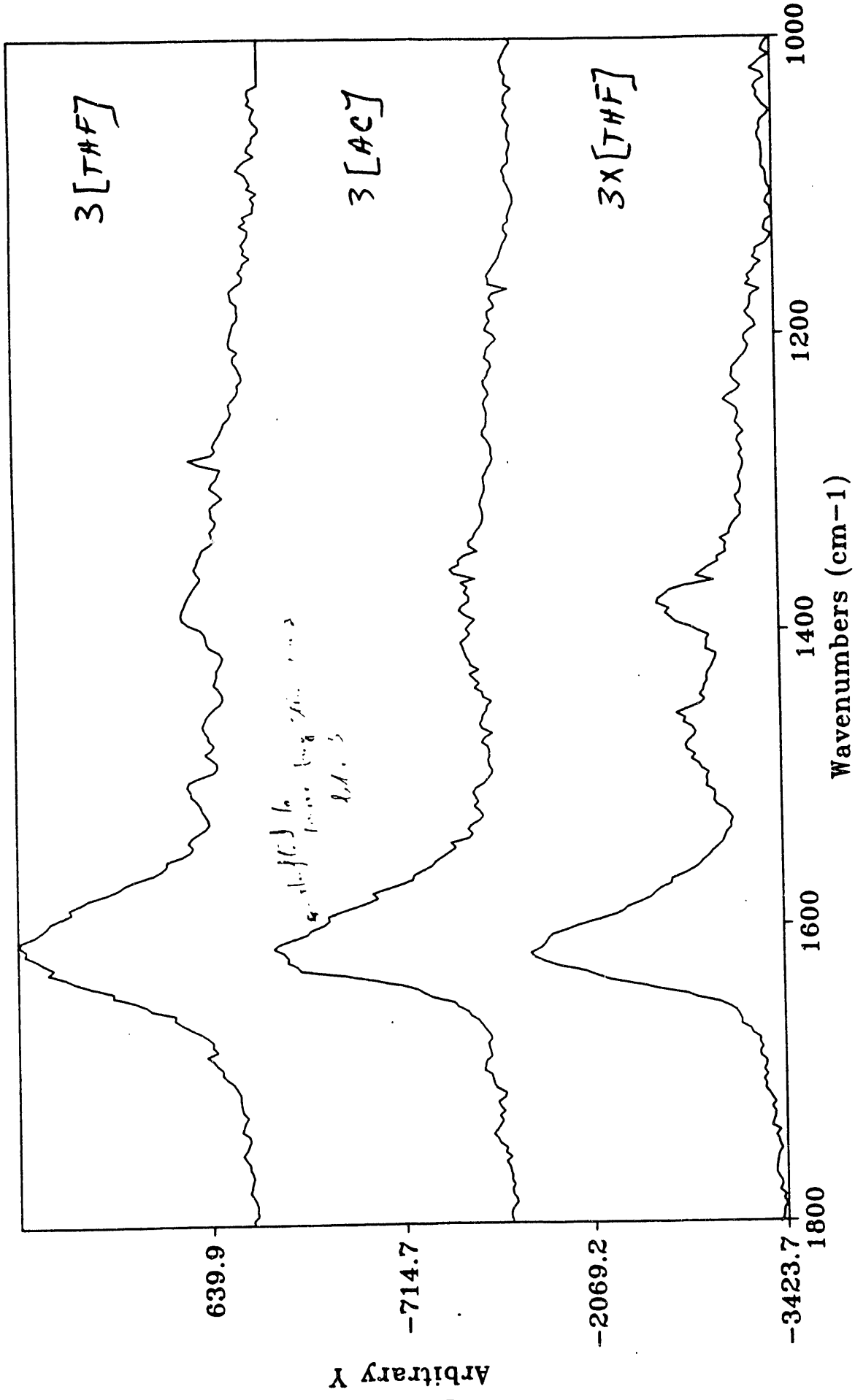
Figure 3B. Sample #2

Res= 1

Figure 3C. Sample #3

10/31/92 07:22

D47D44FF
819150

#4 @ 2285 cm
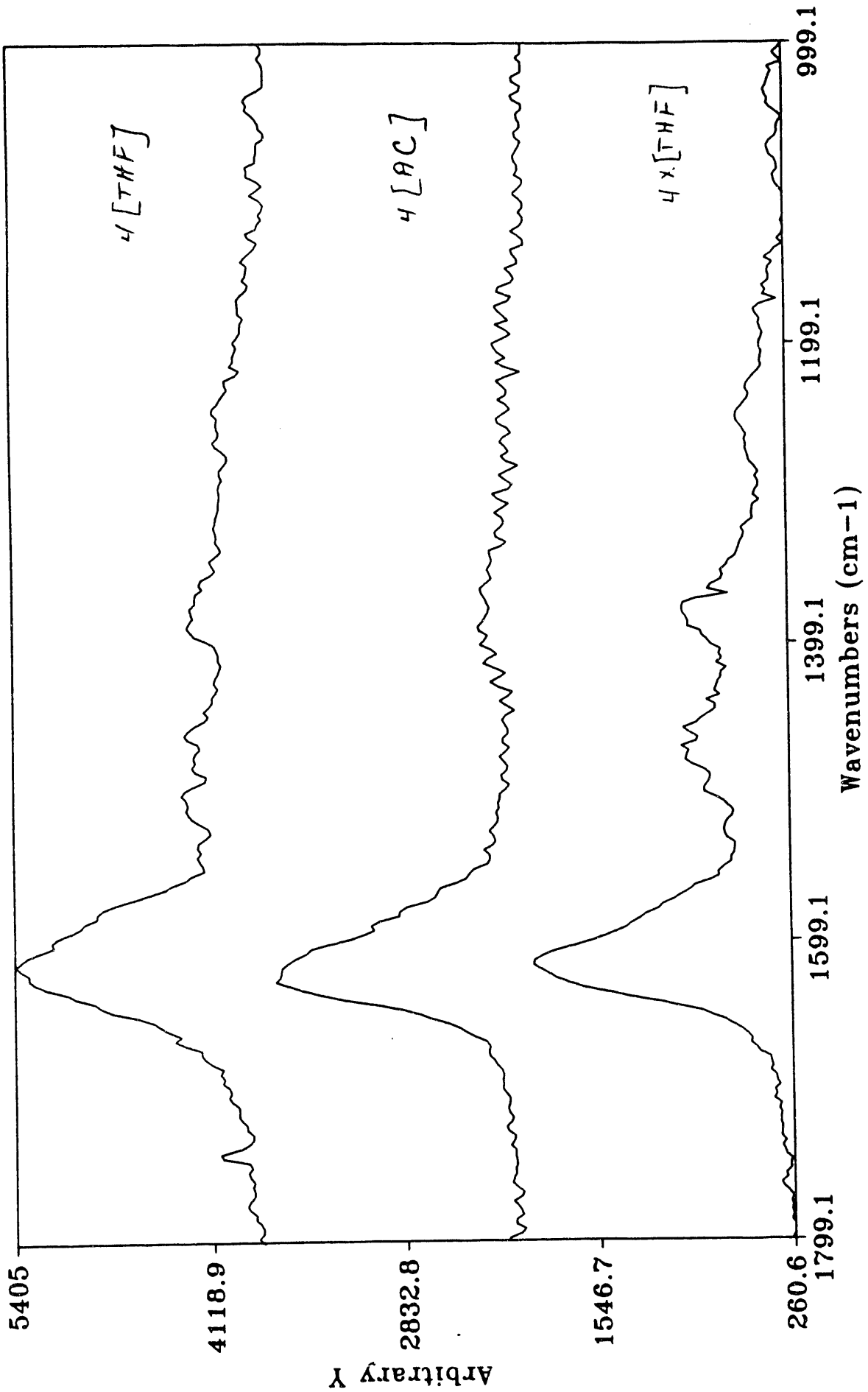
4[THF]

4[AC]

4x[THF]

Wavenumbers (cm-1)

Res= 1   Figure 3D.   Sample #4
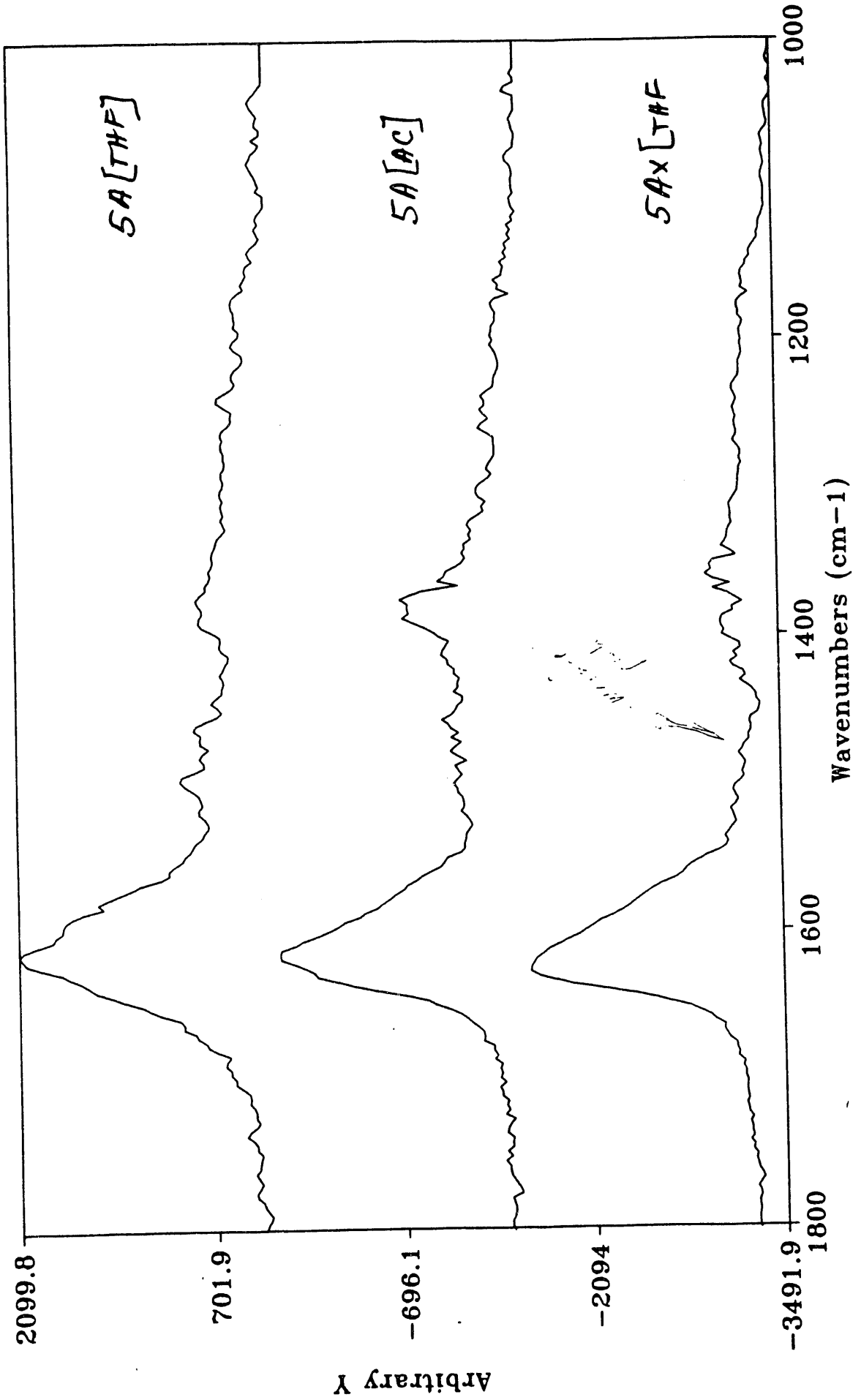
11/05/92 10:02

D84D80F
327660

999.1
1199.1
1399.1
1599.1
1799.1

5405
4118.9
2832.8
1546.7
260.6

Arbitrary Y

26

Figure 3E.   Sample #5A

Res= 1

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D50D44F
819150

27

Figure 3F. Sample #5B
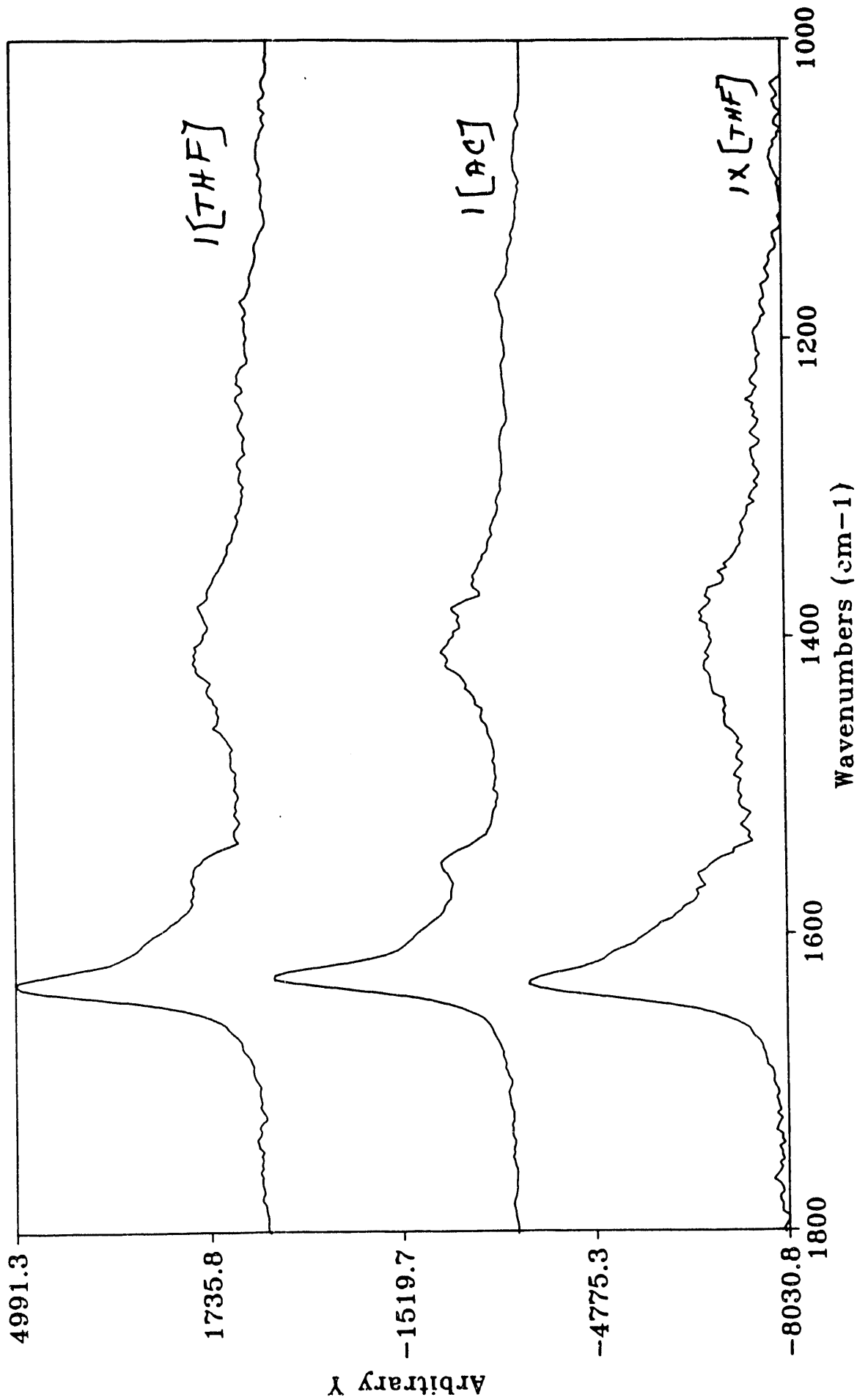
Wavenumbers (cm−1)

Res= 1

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D49D44F
819150

28

Figure 4A.   Sample #1

Res= 1

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D107D106

196596

Figure 4B.   Sample #2

Res= 1

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D108D106

163830

30

Figure 4C.   Sample #3

10/31/92 09:01

Res= 1

D109D106
180213

31

Wavenumbers (cm−1)
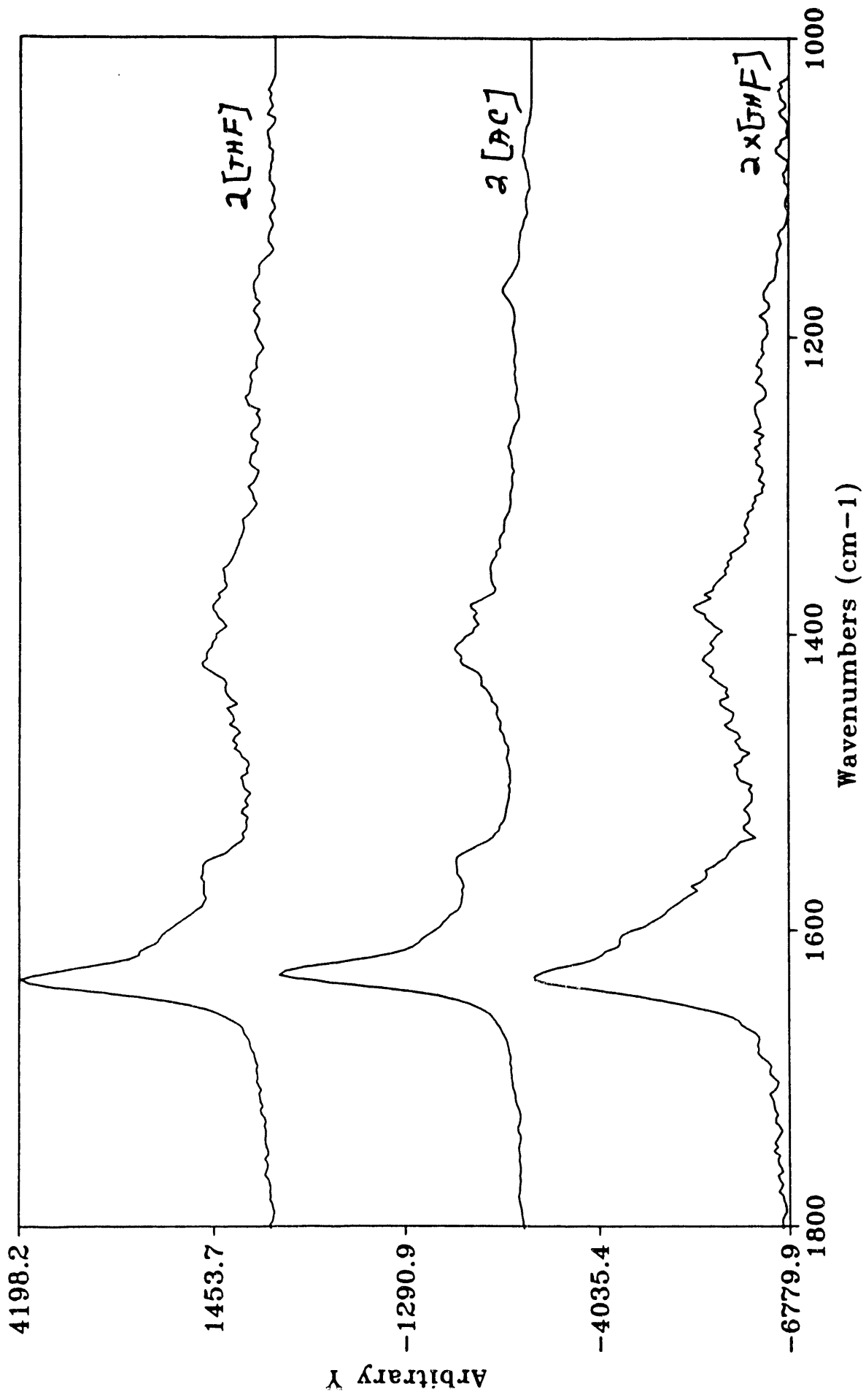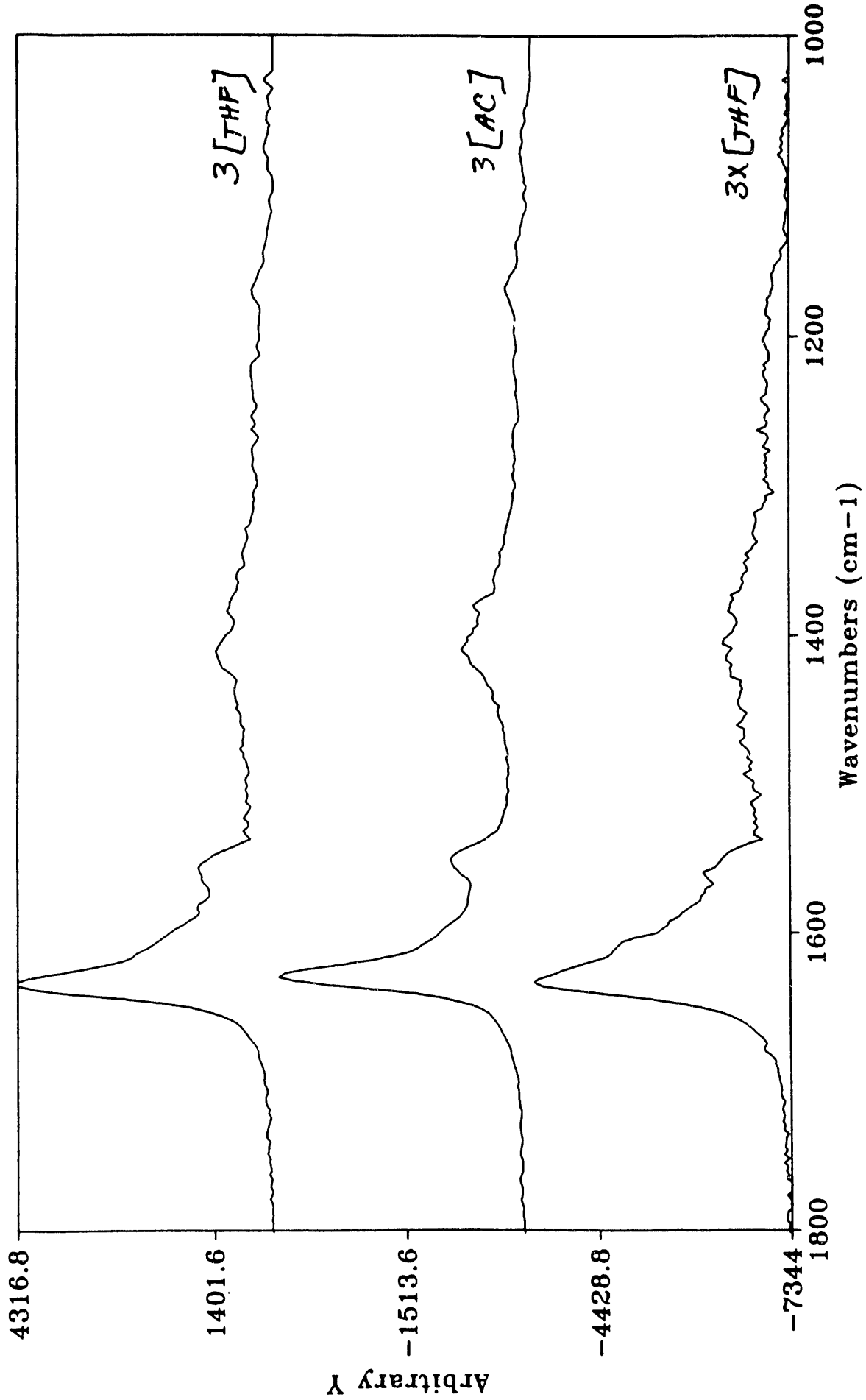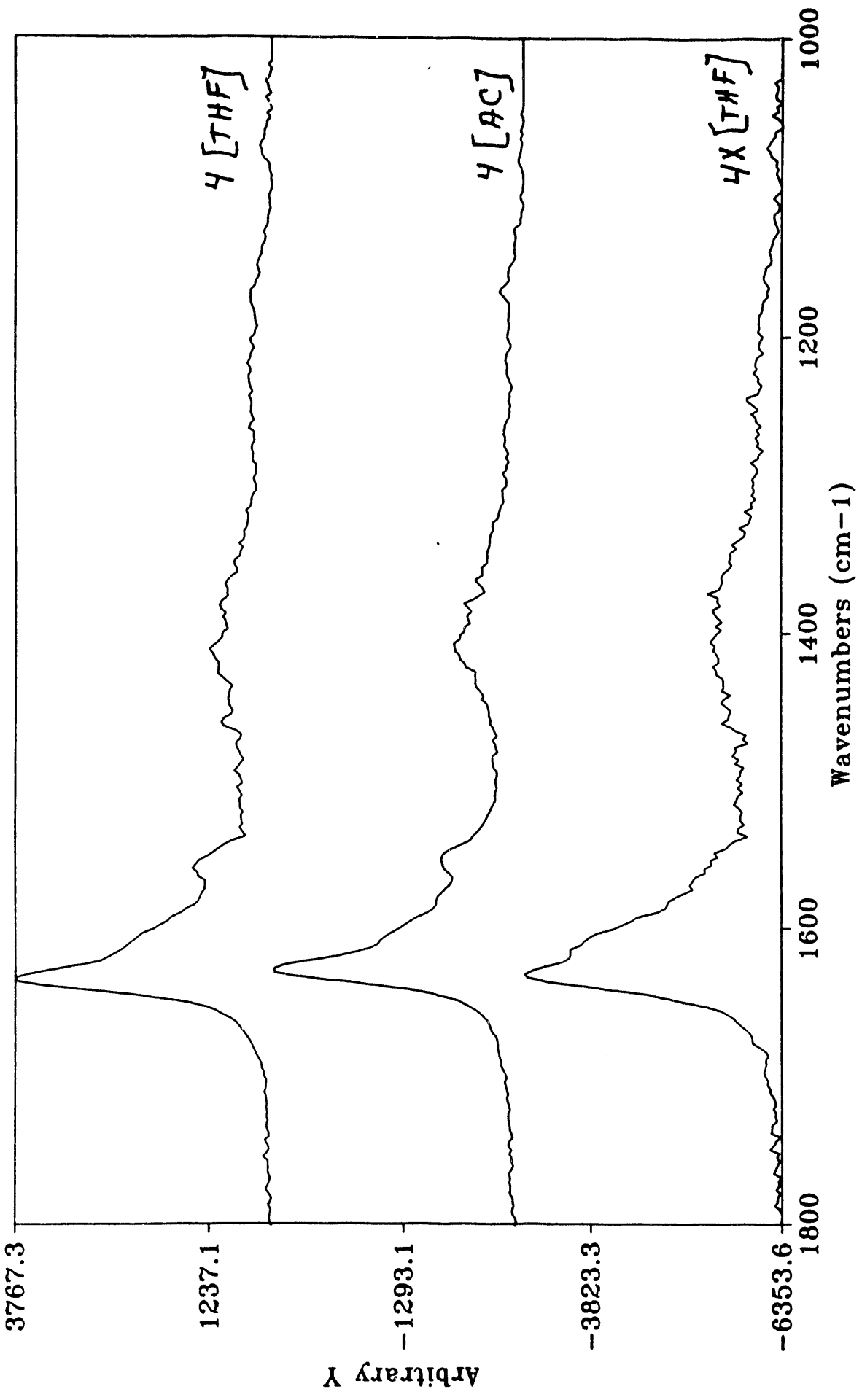
10/31/92 09:08

Res= 1

Figure 4D.   Sample #4

D110D106

163830
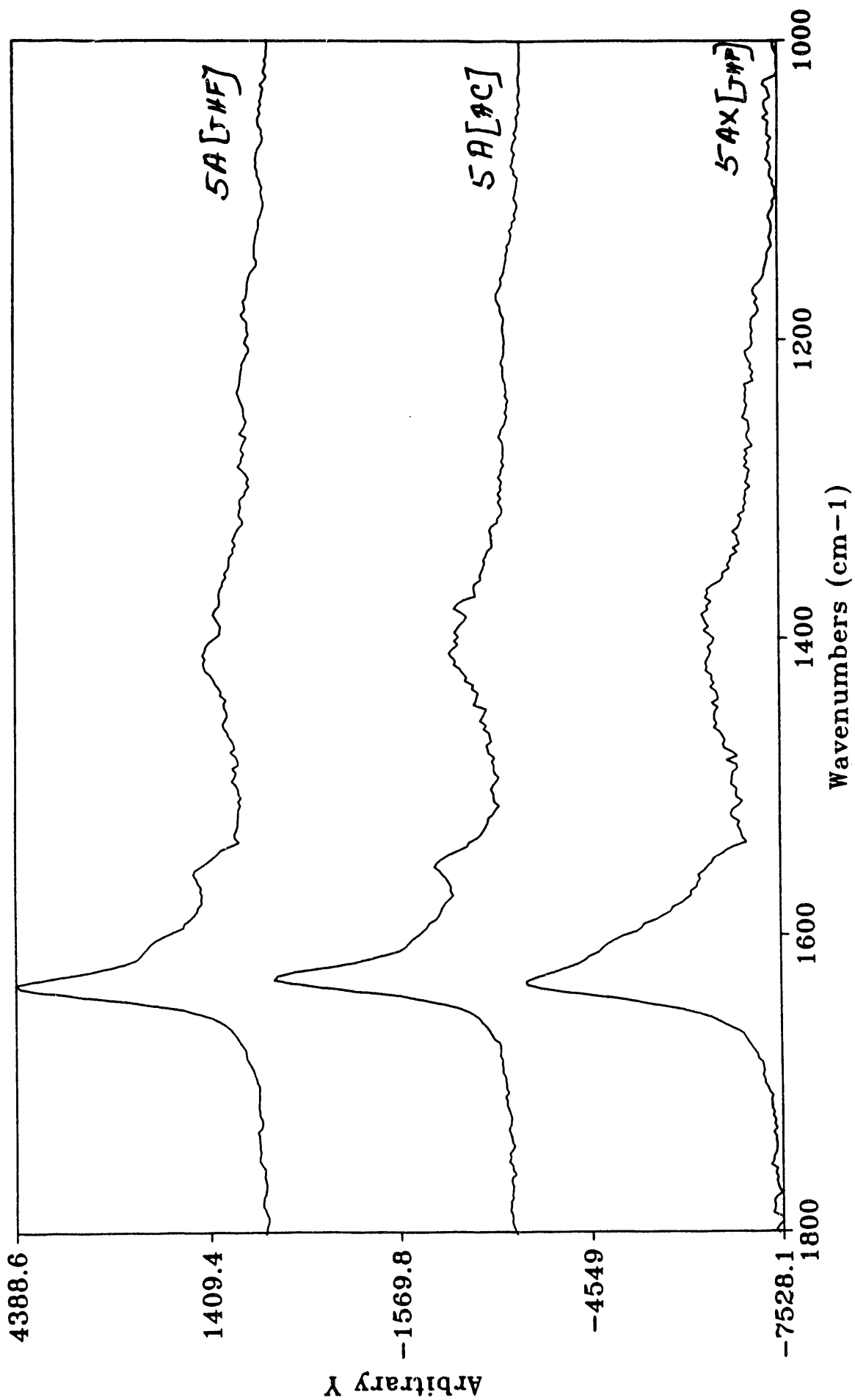
4 [THF]

4 [AC]

4X [THF]

Arbitrary Y

32

Figure 4E. Sample #5A

Res= 1

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Wavenumbers (cm−1)

Arbitrary Y

D111D106

163830

33

5B[THF]

5B[AC]

5Bx[THF]

Wavenumbers (cm−1)

Arbitrary Y

6906

2366.4

−2173.2

−6712.8

−11252

1000

1200

1400

1600

1800
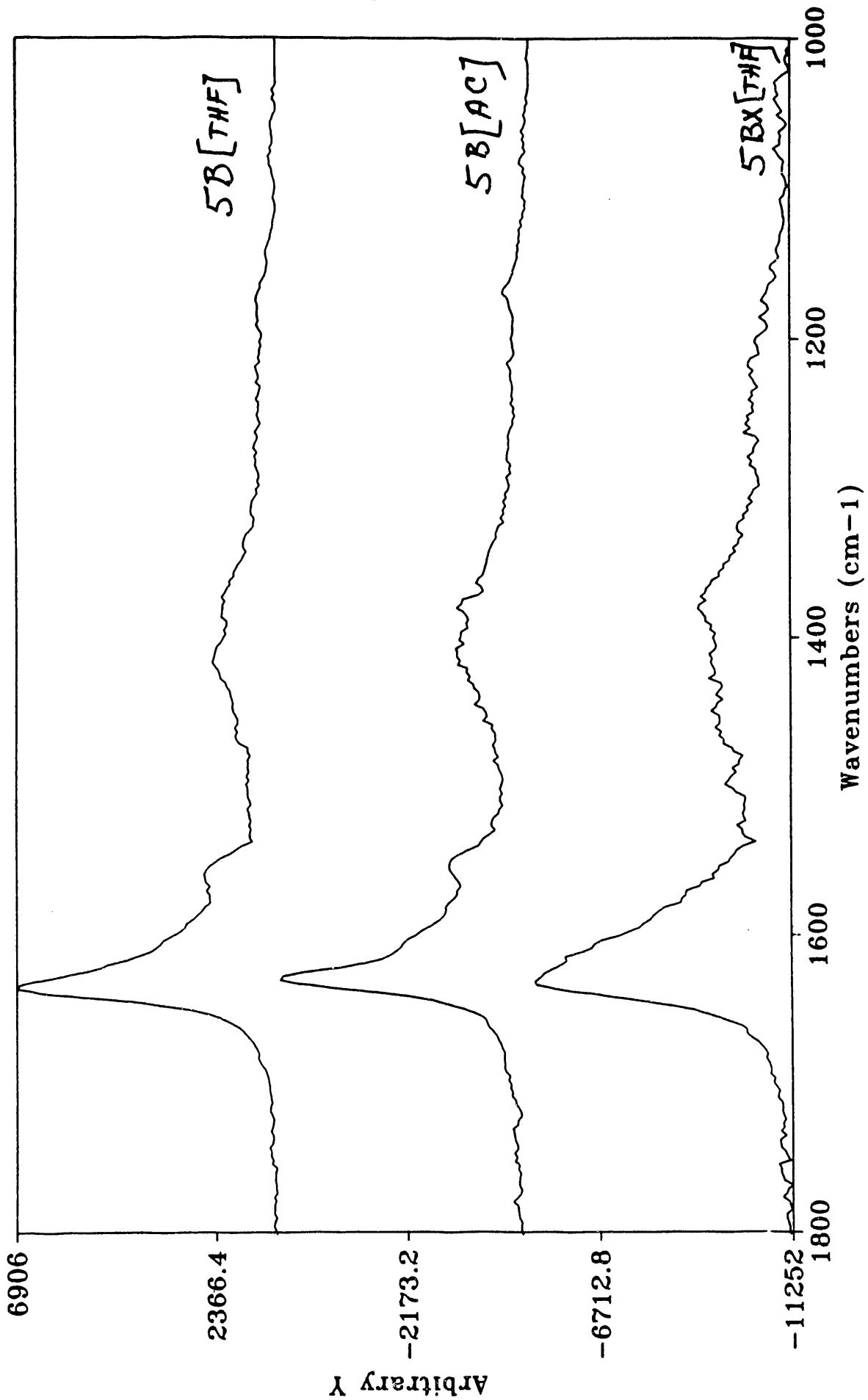
Res= 1

10/31/92 09:30

Figure 4F. Sample #5B

D112D106

278511
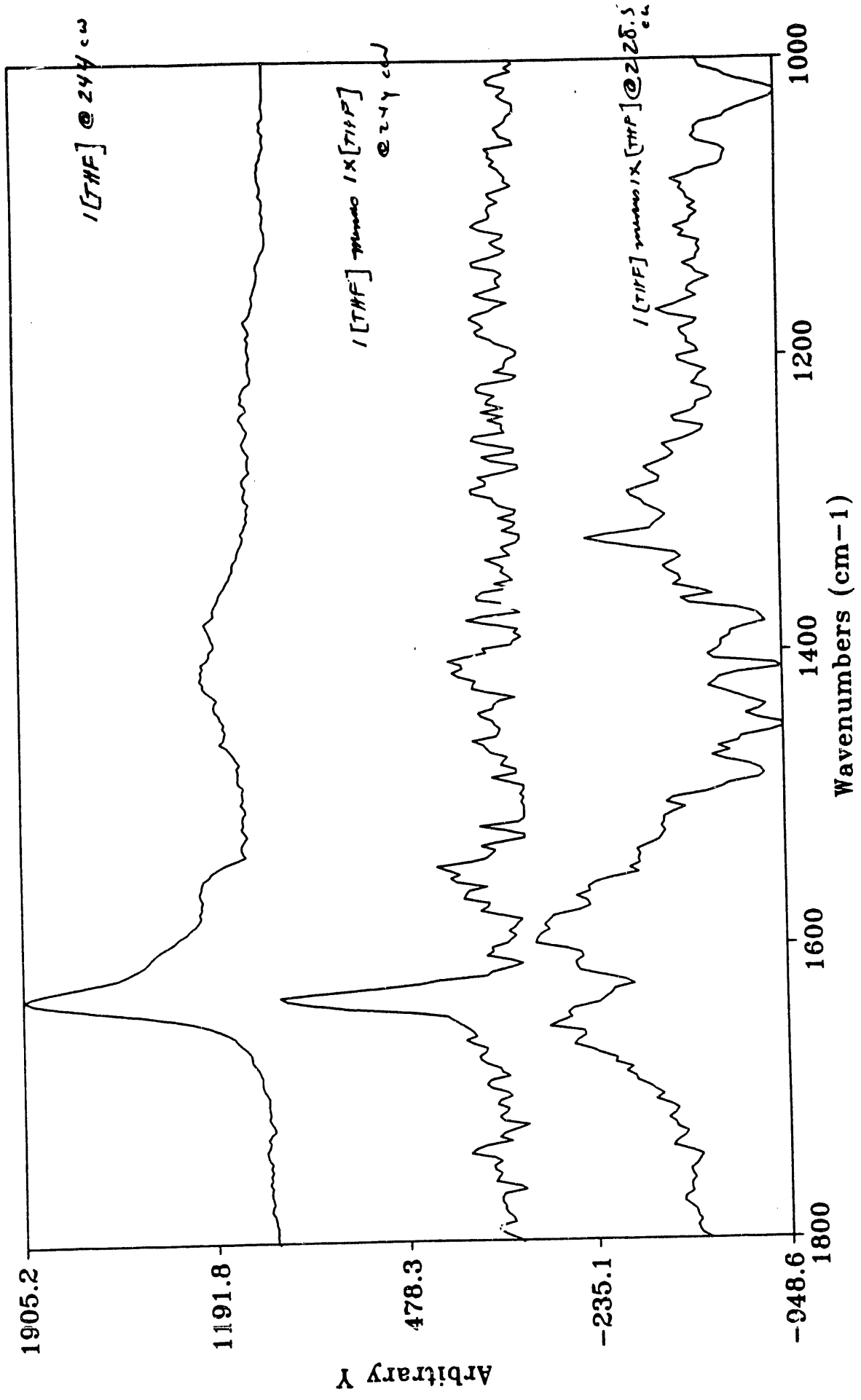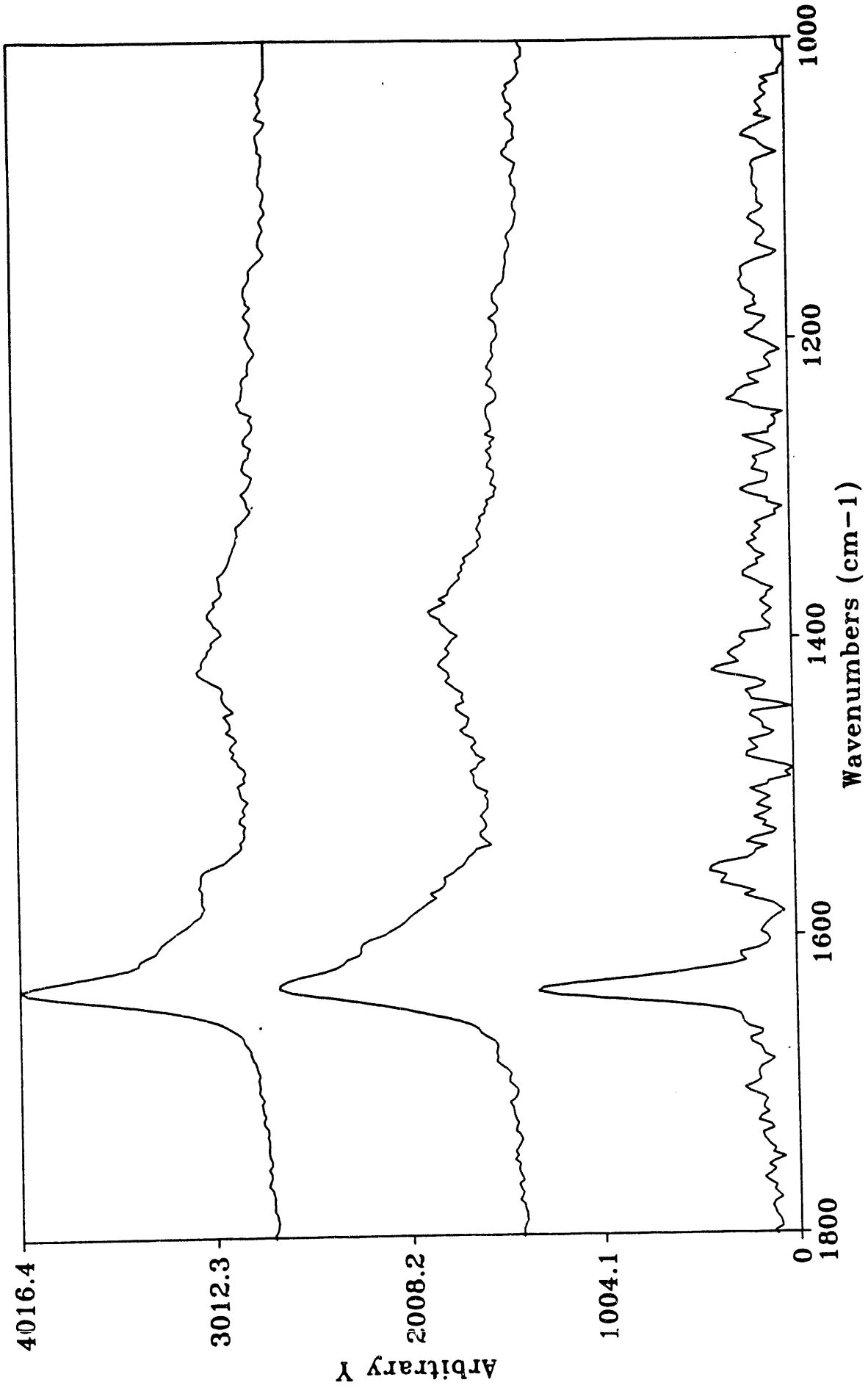
34

Figure 5A.   Sample #1

Res= 1

11/05/92 11:00

107M114
196596

35

[2] - [.000][x7]

GMFl @244

Figure 5B. Sample #2

Res= 1

11/11/92 18:09

Wavenumbers (cm-1)

Arbitrary Y

U2M2X

163830

36

Figure 5C. Sample #5A

$(5\text{-}A) - (0.8)(5Ax)$

@244 cm

5A

diff

5A

Wavenumbers (cm-1)

11/11/92 17:48

Res= 1

U5AM5AX
163830

Arbitrary Y

3384.2

2138.1

892

-354.1

-1600.3

1000

1200

1400

1600

1800

37

[cyclopentadienyl-lithium]
[THF] @244

5B
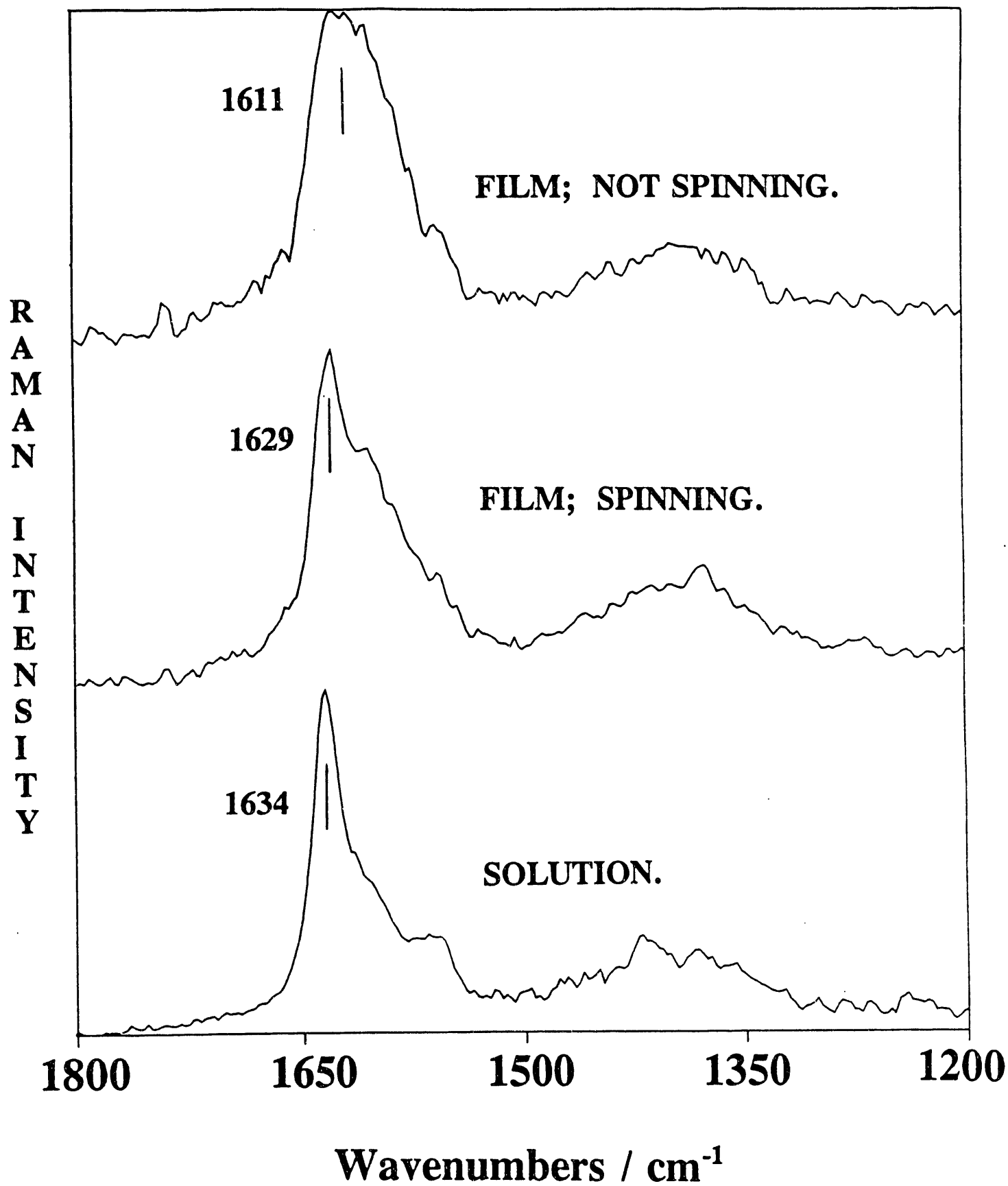
5b

diff
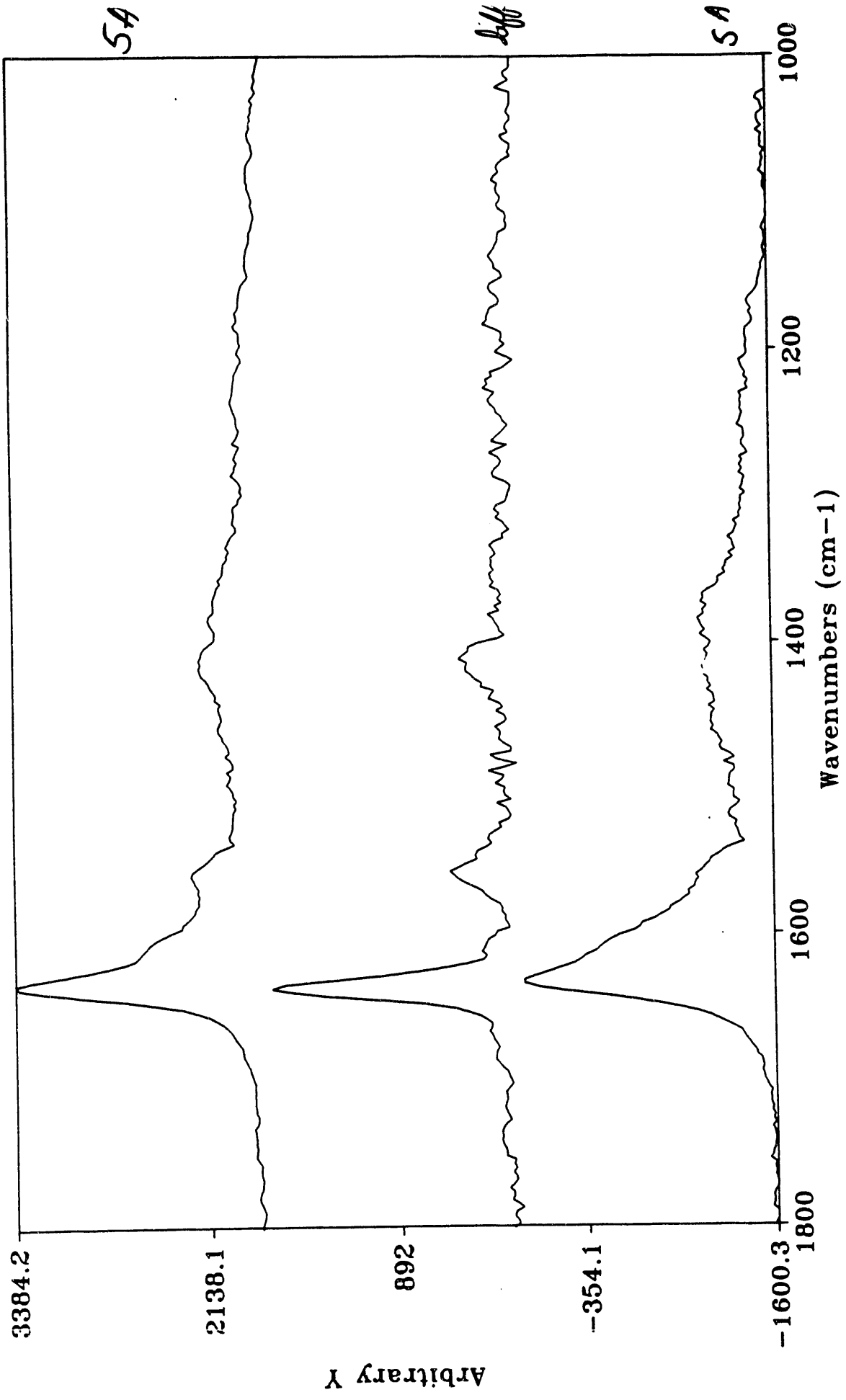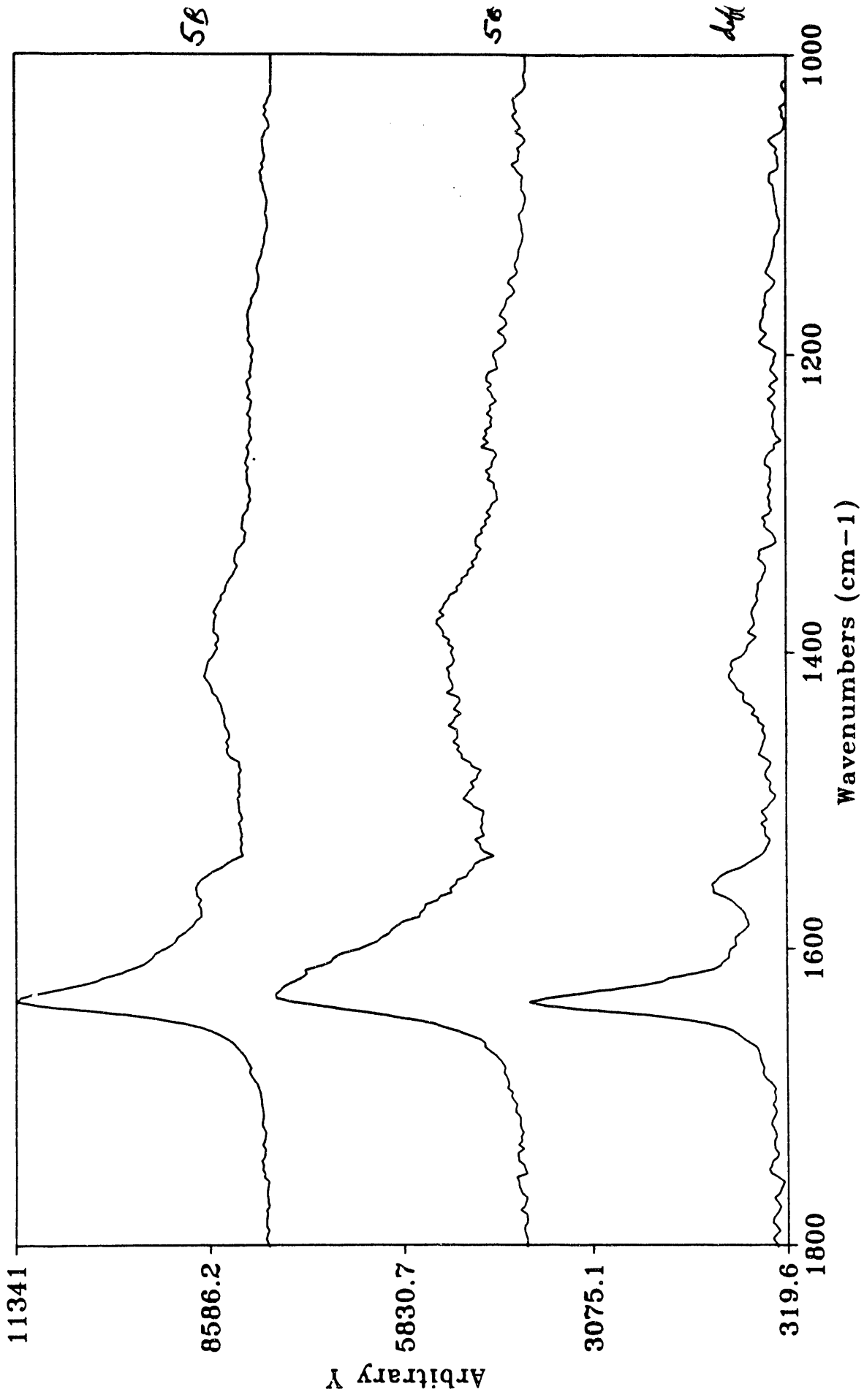
11/11/92 17:58

Res= 1
Figure 5D. Sample #5B

U5BM5BX
2785511

38

Figure 6. Sample #2

END

DATE
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4 / 15 / 93