Coal Liquefaction Process Streams Characterization and Evaluation

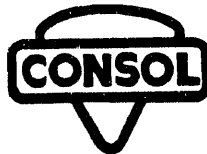## Investigation of the Forms of Sulfur in Five Wilsonville Resid Samples by XAFS and Mössbauer Spectroscopy

Topical Report

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PROJECT ASSESSMENT

Introduction

Under subcontract from CONSOL Inc. (U.S. DOE Contract No. DE-AC22-89PC89883), the University of Kentucky studied the use of X-ray absorption fine structure (XAFS) spectroscopy, specifically the least-squares analysis of the X-ray absorption near edge structure (XANES) region of the K-shell XAFS spectra, for the quantitative analysis of the functional forms of organic sulfur in coal derived materials. The University of Kentucky also studied the use of Mössbauer spectroscopy for characterization of the iron-based sulfur-containing components in the coal derived materials. The full report authored by the University of Kentucky 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 demonstrated the feasibility of using XAFS and Mössbauer spectroscopy for the examination of distillation resid materials derived from direct coal liquefaction. The least-squares analysis of the XANES region of the K-shell XAFS spectra was shown to be a technique which can be used to determine the sulfur forms in coal liquefaction-derived resid samples. The large amount of pyrrhotite in the resid samples (71 to 99% $\pm$10% of the total sulfur) interfered with the precise quantitative analysis of the organic sulfur. However, a spectral subtraction routine was successfully used to provide semi-quantitative results for sulfur species other than the pyrrhotite.

Mössbauer spectroscopy, considered a more accurate method than XAFS for the quantitative analysis of inorganic iron-sulfur species (pyrite, pyrrhotite, iron sulfates), was successfully used to speciate these materials in the coal liquefaction resids. Further application of XAFS and Mössbauer spectroscopy as process development tools appears justified by these results.

Program Description

This report describes the work performed at the University of Kentucky 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 Kentucky used XAFS and Mössbauer spectroscopy to analyze five $850°F^+$ distillation resids. The samples were composite $850°F^+$ resids of samples taken over long periods of single runs from the Wilsonville pilot plant. These are solids at room temperature, and contain THF-soluble and -insoluble organics and mineral matter. Samples were taken from two locations: between the first- and second-stage reactors and after the second-stage reactor. These samples are expected to represent different extents of coal liquefaction. Two major processing parameters were varied among the Wilsonville runs: feed coal and reactor configuration (thermal/catalytic vs. catalytic/catalytic).

The experimental details for the sulfur XAFS procedure and the Mössbauer spectroscopy procedure are described on page 2 of the attached report.

Participant's Major Findings

The following principal observations for the application of XAFS and Mössbauer spectroscopy to coal liquefaction resids were reported by the University of Kentucky. An expanded discussion can be found in the attached report, pages 2 through 6.

Pyrrhotite was the dominant sulfur species in all five resids, accounting for 71 to 99% ($\pm$10%) of the total sulfur in the samples. The large pyrrhotite peak dominated the XANES spectra and partially interfered with regions of the spectra, where the s$\rightarrow$p peaks for thiophene and organic sulfide occur. To circumvent the limitations imposed by the pyrrhotite interference, a least-squares fit of the spectra was performed to quantify the sulfur in three broad categories: pyrrhotite, unoxidized organic sulfur, and sulfate (instead of the usual nine or so categories). This approach indicated that the samples contained 0 to 23% ($\pm$5%) unoxidized organic sulfur and 1 to 6% ($\pm$3%) sulfate sulfur in addition to the pyrrhotite sulfur. In an attempt to better quantify the sulfur species, the pyrrhotite was mathematically subtracted from the spectra and then the pyrrhotite-subtracted spectra were analyzed by the least-squares fitting method. The XANES spectrum of the one resid produced from Wyodak coal was used as the reference pyrrhotite spectrum because the original XANES analysis showed that the sulfur in that sample was virtually all in the form of pyrrhotite. This approach yielded semi-quantitative values for sulfidic, thiophenic, sulfoxide, sulfone and sulfate sulfur in the remaining four resids. Although the results are only semi-quantitative, some trends can be observed in the data. For example, a comparison of the Illinois No. 6 coal-derived interstage resids from different runs shows that a much higher proportion of the non-pyrrhotite sulfur is thiophenic sulfur in the resid produced by a thermal first stage (Run 250) than the resid produced from a catalytic first stage (Run 257) (78 vs. 38%, $\pm$20%). The non-pyrrhotite sulfur in the one sample from Pittsburgh seam coal is almost entirely thiophenic (81% $\pm$20%) and sulfate (15% $\pm$10%).

The Mössbauer spectra of all five samples were similar. A least-squares fit was made of each spectrum and the iron-containing compounds were identified and measured. Pyrrhotite was found to be the dominant iron-bearing phase present, accounting for 84 to 95% +/- 2% of the total iron. The vacancy content of the pyrrhotite ($Fe_{(1-x)}S$) was found to be 6 to 8%, significantly lower than the 9 to 12.5% of most mineral pyrrhotites. Several other iron phases were observed. A ferric phase, which may be either an iron oxide or iron contained in a clay-derived silicate phase, was found in all five resids. Ferrous sulphate (most likely szomolnokite, $FeSO_4 \cdot H_2O$), which may have formed by oxidation of the pyrrhotite after liquefaction, was found in three of the samples. Magnetite was found in the one Wyodak coal derived sample.

The results of the XANES and Mössbauer analyses of the five resid samples were compared to the results of similar analyses of the Argonne Premium coals which correspond most closely to the feed coals used in the lique-faction processing runs. The Argonne coals were examined previously by the researchers at the University of Kentucky. The University of Kentucky observed that the iron species in the Wyodak coal resid must be primarily derived from the iron catalyst used in the processing run because the parent coal has a very low iron content. Additional discussion comparing the resids and coals can be found on pages 4 through 5 of the attached report.

CONSOL Evaluation

The sulfur XAFS/XANES and Mössbauer techniques were shown to be potentially useful for the quantitative speciation of sulfur forms in direct coal liquefaction resid samples. The dominant pyrrhotite peak in the XAFS spectra partially interfered with the organic sulfur region and reduced confidence in the accuracy of the quantitative data. These experiments demonstrate that for accurate quantitative speciation of the organic sulfur forms in coal-derived resids, the XAFS/XANES technique should be performed on the inorganic-free portion of the sample. The Mössbauer technique clearly showed that pyrrhotite was the dominant iron-bearing species present in the resids and provided the stoichiometry of the pyrrhotite. Other iron species were also detected, including ferric oxides or silicates, ferrous sulfate and magnetite.

The Mössbauer instrument used in these studies cost approximately $50,000. It requires approximately one day to prepare and collect data for a single sample by Mössbauer spectroscopy. The sulfur XAFS experiments were conducted at the National Synchrotron Light Source at Brookhaven National Laboratory. Approximate time requirements are 1-2 hr to prepare a sample and about 1 hr to collect data. Cost per sample is approximately $1000. Data acquisition and interpretation for both methods require a considerable amount of time (on the order of a few hours to one week) and the expertise of a skilled professional.

Further Development
The interference by pyrrhotite in the quantitative determination of the organic sulfur species by XANES indicates that future applications would be better performed with only the organic component of the resid (e.g., the solvent-soluble portion of the resid). The XAFS technique also can be used for the direct speciation of other elements, such as nitrogen and possibly oxygen. Exploration of the applicability of the technique for the quantitative analysis of these heteroatomic species in coal liquids is recommended.

Participant's Statement of Work
X-ray absorption fine structure (XAFS) Spectroscopy has been demonstrated to be a powerful technique for the investigation of sulfur in coal and coal derivatives. The least-squares analysis of the X-ray absorption near edge structure (XANES) region of the K-shell XAFS spectra provides a quantitative analysis of the functional forms of the sulfur. Mössbauer spectroscopy has found numerous applications in coal science, principally for its ability to characterize complex samples containing iron-based components. These techniques have not, however, been demonstrated widely for their ability to answer questions pertaining to the chemistry of coal conversion. As such, they fit well within the scope of the participants program.

The application of XAFS and Mössbauer spectroscopy to a small sample set (5 samples) will allow a demonstration of the value of these techniques for the examination of the sulfur compounds in coal liquefaction-derived

resids. XAFS will allow for a quantitative measurement of the sulfur forms in the samples. Since XAFS has reduced sensitivity for the iron-based inorganic sulfur forms, Mössbauer will be used to supplement the XAFS data with quantitative measurements of the iron-based inorganic sulfur forms. This technique for the quantitative determination of sulfur forms may be useful to characterize resids in support of a study of resid reactivity. These samples have been selected so that the utility of the technique for this purpose can be assessed. The samples will be supplied to the University of Kentucky 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 five samples are 850°F$^+$ distillation residual materials and contain insoluble organic material (IOM) and ash. Sample size will be at least 3 g. The five resid samples will be brittle pitch-like materials that will be supplied as approximately minus 60-mesh powder.

FINAL REPORT

INVESTIGATION OF THE FORMS OF SULFUR IN FIVE WILSONVILLE RESID SAMPLES BY XAFS AND MÖSSBAUER SPECTROSCOPY

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EXECUTIVE SUMMARY

The forms of sulfur in five Wilsonville resid samples have been investigated by XANES spectroscopy and Mössbauer spectroscopy. Three of the samples were obtained from liquefaction runs using Illinois #6 coal, and one each from runs using Pittsburgh and Wyodak coals (Table 1).

Pyrrhotite is the dominant sulfur-containing compound in all five resids. The Mössbauer results show that from 84 to 95% of the iron in the samples is contained in pyrrhotite ($Fe_{(1-x)}S$, with x = 6 - 8%), with minor amounts of ferrous sulfate and other phases present (Table 4). The raw sulfur K-edge XANES spectra were analyzed into three components; pyrrhotite, unoxidized organic sulfur, and sulfate. On the basis of this analysis, pyrrhotite contained from 71 to 99% of the sulfur in the resids, while unoxidized organic and sulfatic forms accounted for up to 23% and 6% of the sulfur, respectively (Table 2).

The dominant phase, pyrrhotite, exhibited strong absorption features in the region of the XANES where the s→p peaks for thiophene and organic sulfide occur, making it difficult to carry out a meaningful analysis of the functional forms of unoxidized organic sulfur. An attempt to physically separate the pyrrhotite from the organic matrix of the resid was not successful. Therefore, a mathematical procedure of subtracting the pyrrhotite XANES from the total resid XANES was developed. The resulting pyrrhotite-subtracted spectra were then analyzed. The results (Table 3) indicated that both sulfidic and thiophenic sulfur functional forms were present in the Illinois #6 resid samples, with thiophenic sulfur being dominant, while only thiophenic sulfur is present in the Pittsburgh seam resid. Too little organic sulfur is present in the Wyodak-Anderson resid to be analyzed by this method. While the accuracy of the XANES analysis for these pyrrhotite-subtracted spectra is rather poor, the results seem to be reasonable on the basis of previous work on the alteration of sulfur forms resulting from pyrolysis.

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I. INTRODUCTION

In recent years, it has been shown that all of the major forms of sulfur in coal can be speciated by XAFS spectroscopy. Two principal approaches have been developed, both of which deal with analysis of the X-ray absorption near edge structure (XANES) region of the XAFS spectrum. Gorbaty and co-workers have developed a third derivative treatment of the XANES which allows the relative amounts of thiophenic and sulfidic sulfur to be determined [1,2]. Our group has developed a direct least squares analysis treatment of the XANES which allows up to nine forms of sulfur to be quantitatively determined [3-5]: pyrrhotite, pyrite, elemental sulfur, organic disulfide, organic sulfide, thiophenic sulfur, sulfoxide, sulfone, and sulfate. In the case of the inorganic iron-sulfur phases (pyrite, pyrrhotite, iron sulfates), however, Mössbauer spectroscopy is normally a more accurate method of analysis [6]. Consequently, for samples containing both organic and inorganic sulfur species, we usually employ both techniques.

In the current study, five resid samples from the Wilsonville pilot plant have been investigated. These samples are listed in Table 1. They include a second stage product resid from a catalytic/catalytic (C/C) run that utilized an Illinois #6 coal, and four interstage resid samples from runs using Illinois #6 (T/C and C/C), Pittsburgh seam (C/C), and Wyodak coals (C/C). Pyrrhotite was the dominant sulfur-containing phase observed in all samples, representing from 70 to 100% of the total sulfur. The large amount of pyrrhotite present hampered our efforts to obtain accurate results

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for the percentages of organic and other sulfur forms present. However, by employing spectral subtraction procedures, it was possible to obtain at least semiquantitative results for the sulfur species other than pyrrhotite. As discussed in the remainder of the report, thiophenic and sulfatic sulfur are the dominant secondary forms of sulfur present.

II. EXPERIMENTAL PROCEDURE

The Mössbauer spectrometer used in these experiments was a constant acceleration spectrometer of standard design [6]. The radioactive source consisted of 50-100 mCi of ^{57}Co in a Pd matrix. The Mössbauer samples were in the form of powder samples mounted in plexiglass compression holders. All spectra were obtained at room temperature. Since the room-temperature Mössbauer spectra were readily interpretable, it was felt that spectra obtained at other temperatures were not necessary.

The sulfur XAFS experiments were conducted at beamline X-19A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. X-19A maintains the x-ray path from the synchrotron to the monochromator to the experimental hutch entirely in the storage ring vacuum in order to minimize beam absorption. Additionally, a helium pathway was maintained for the beam within the hutch, to further minimize unnecessary absorption by air. Electron currents in the ring were typically 100-200 mA. The x-ray energy was varied from approximately 100 eV below the sulfur K-shell absorption edge (2472 eV) to 400 eV above the edge using a double crystal Si(111) monochromator. The solid resid powder samples were loaded in thin (6 micron) mylar bags and fluorescent sulfur XAFS spectra were obtained using a Stearn-Heald type of detector [7].

III. RESULTS AND DISCUSSION
III.1 XANES Results

The suite of sulfur XANES spectra of all samples is shown in Figure 1. The uppermost spectrum, obtained from the first stage Wyodak resid, is representative

of essentially pure pyrrhotite, the only sulfur species present in this sample in significant quantity. By comparison of this XANES to the other spectra, it is seen that a large, broad absorption feature in the pyrrhotite spectrum overlaps and obscures most of the other XANES peaks. This makes it difficult to accurately fit the unoxidized organic sulfur XANES peaks, which occur between 0 and 3 eV [3-5]. Nevertheless, all of the raw XANES files have been fitted and the results do not appear to be unreasonable. Typical fits are shown in Figures 2 and 3; all spectra are compiled in Appendix A. As discussed elsewhere [3,4], the XANES are fitted to a series of peaks (50% Lorentzian, 50% Gaussian) and an arctangent function. The peaks represent s→p photoelectron transitions and scattering peaks, while the arctangent function represents transitions of the photoelectrons to the continuum. The s→p peaks have characteristic energies and can be used to identify different sulfur forms. The areas under these peaks can then be used to determine the relative amounts of sulfur contained in each sulfur form identified [3-5]. Unfortunately, because of the large, broad maximum contributed by the pyrrhotite spectrum for all of these samples, the accuracy of this model is substantially decreased. Referring to Figures 2 and 3, the s→p peaks derived from pyrrhotite (-1.5 eV), thiophenic sulfur (1.3 eV), and sulfatic sulfur (10.0 eV) are seen to be fairly well-resolved. Peaks from elemental sulfur (0.0 eV) and from organic sulfur species such as polysulfidic sulfur (0.2-0.4 eV), (mono)sulfidic sulfur (0.4 - 0.7 eV), sulfoxide (3.4 eV), and sulfone (7.5 - 8.0 eV), which, if present at all, would be expected to be much less intense than peaks from pyrrhotite, thiophene, or sulfate in resid samples, are very difficult to determine accurately from the current data because of interference from the pyrrhotite XANES. Consequently, in the data summary for the resid samples presented in Table 2, we have not attempted to subdivide the organic sulfur species, but have simply presented the sulfur percentages as divided between three dominant components: pyrrhotite; unoxidized organic sulfur (believed to be principally thiophene), which would also include any elemental sulfur; and sulfate.

Two attempts were made to decrease the pyrrhotite signal in order to get a better speciation of the organic sulfur. One effort was aimed at simply physically

separating the pyrrhotite from the resid samples. Samples were crushed to -200 mesh and centrifuged in liquids having specific gravities of 1.5 and 2.5. While this procedure is usually successful in separating pyrite from coal, it was completely ineffective in separating pyrrhotite from resid. The centrifuge tubes were uniformly black after centrifugation and no separation was effected. Perhaps the pyrrhotite and other ash particles are so uniformly coated by the resid that there is no tendency for fracture to occur along the mineral-organic matrix boundary, as there is in coal.

In the second attempt, the pyrrhotite contribution to the sulfur XANES spectrum was removed mathematically. As mineralogical specimens of pyrrhotite are known to exhibit significant variation in composition and crystal structure and generally do not simulate well the pyrrhotite found in liquefaction experiments, it was decided to use the sulfur K-edge spectrum of the Wyodak resid as the standard for the mathematical subtraction. Hence, the spectrum of the Wyodak resid, run 258, which was essentially all pyrrhotite, was weighted appropriately and subtracted from the other spectra. The weighting was varied until the pyrrhotite s→p peak at -1.5 eV was reduced as closely as possible to zero. Typical least squares fits of these pyrrhotite-subtracted XANES spectra are shown in Figures 4 and 5; all such spectra are shown in the compilation in Appendix A. The results of the least squares analyses are given in Table 3. While the sulfur form percentages in Table 3 are not unreasonable, they are considered semi-quantitative. In particular, the sulfide and sulfoxide components are in regions of the spectra where incorrect subtraction procedures could cause substantial errors.

III.2 Mössbauer results

The Mössbauer spectra of all five samples were quite similar and clearly showed pyrrhotite to be the dominant iron-bearing phase present. Typical spectra are shown in Figure 6; all spectra are included in the compilation in Appendix A. The solid curves are the least squares fits to the spectra, which were modeled by three six-peak magnetic hyperfine spectra and one or two quadrupole doublets. The locations and relative intensities of the peaks from each of these components is indicated by the bar diagrams in Figure 6.

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From the relative areas under the peaks of each fitted spectral component, the approximate percentages of the total iron contained in each phase can be determined [6]. The results of this analysis are given in Table 4. Also given in Table 4 are the observed Mössbauer parameters for each component. Pyrrhotite ($Fe_{(1-x)}S$) contributes three magnetic hyperfine components with magnetic hyperfine fields (H) of approximately 311, 289, and 264 kiloGauss. These values and the quadrupole splitting (Q.S.) and isomer shift (I.S.) parameters are in agreement with those previously reported for pyrrhotite. The standard deviations are approximately as follows: H - ± 2 kG; I.S. - ± 0.02 mm/s; Q.S. - ± 0.02 mm/s; %Fe - ± 2%. It is seen that the total percentage of the resid iron contained in pyrrhotite ranges from 84% to 95%. The relative percentages of the three pyrrhotite magnetic components indicate that the vacancy content of the $Fe_{(1-x)}S$ phase is $x = 6 - 8\%$. This is a significantly lower vacancy content than is found in most natural pyrrhotites in which x is normally between 9 and 12.5%.

While pyrrhotite is the dominant iron-bearing phase, minor amounts of two other phases are also observed: a ferric phase, which may be either an iron oxide or iron contained in a clay-derived silicate phase; and ferrous sulfate, most likely szomolnokite, $FeSO_4.H_2O$. The latter phase may have formed from the pyrrhotite due to exposure to air since the liquefaction run was made.

III.3 Previous Sulfur Speciation Results for the Argonne Premium Coals.

In previous work [3,8], we have investigated the sulfur forms in the Argonne premium coals by XANES and Mössbauer spectroscopy. The results of those studies for the Pittsburgh seam, Illinois #6, and Wyodak coals are given in Table 5. It is seen in Table 5b that pyrite is the only significant iron phase in the Pittsburgh and Illinois coals, while the Wyodak coal contains 26% of its iron in siderite and 75% in pyrite. It is clear that pyrite is devolatilized to form pyrrhotite during liquefaction. The siderite apparently transforms to a mixture of magnetite and pyrrhotite, the latter forming by reaction with H_2S. Such results have been reported previously [9]. It should be noted, however, that 2 wt% of iron oxide plus sulfur was added for the Wyodak liquefaction run. Since the Wyodak coal is very low in pyrite and total iron

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content, it is clear that most of the pyrrhotite and iron oxide observed in the Mössbauer spectrum of the resid is derived from the reaction products of the added iron catalyst.

The XANES results show sulfide and thiophene to be the only significant forms of organic sulfur present in the Argonne Premium coals. They also indicate no sign of sulfur oxidation. For the Illinois and Wyodak coals sulfidic and thiophenic sulfur account for about 35 and 65% of the organic sulfur, respectively, while the corresponding values for the Pittsburgh coal are 27 and 73%. On the basis of a previous study of the alteration of sulfur distribution resulting from pyrolysis [5], the sulfidic component would be expected to decrease more than the thiophenic component during liquefaction. For reasons given above, however, our results for the relative amounts of sulfidic and thiophenic sulfur in the resids are not considered to be accurate enough to reach any conclusions on this point. It is seen, however, from a comparison of Table 2 and Table 5a, that a significantly larger percentage of the sulfur is inorganic (pyrrhotite) in the resids than in the coals. It is apparent that organic sulfur is being released during liquefaction, while the inorganic sulfur is apparently stabilized at approximately half its initial value as pyrrhotite.

IV. RECOMMENDATIONS

Examination of the resids by sulfur K-edge XAFS spectroscopy showed that the least-squares method for determining sulfur forms was not very accurate for organic sulfur forms because of the dominance of the inorganic sulfur (pyrrhotite) in the resid. If improved accuracy on the organic sulfur functional forms in the resids is desired, there are several possible approaches. One would be to examine organic-rich extracts obtained from the resids by extraction with either pyridine or with tetra-hydrofuran (THF). A second possibility is to develop a method of removing the pyrrhotite from the resid by physical means. A final method would be to prepare new samples in bench scale tests from a coal of negligible pyrite content, such as the DECS-17 or DECS-6 Blind Canyon sample in the Penn State coal sample bank.

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Table 1. Resid samples investigated by XANES and Mössbauer spectroscopy.

Ref. No.	Coal Feed	Source/Conditions	Comments
1	Illinois 6	W; Run 250; T/C	Interstage
2	Illinois 6	W; Run 257; C/C	Second-Stage Product
3	Illinois 6	W; Run 257; C/C	Interstage
4	Pittsburgh	W; Run 259; C/C	Interstage
5	Wyodak Anderson	W; Run 258; T/C	Interstage

Note: All samples are 850°F⁺ distillation resids; C/C = Catalytic/Catalytic; T/C = Thermal/Catalytic; W = Wilsonville

Table 2. Percentages of the total resid sulfur contained in three principal forms determined by analysis of the sulfur XANES.

Sample	Pyrrhotite (± 10%)	Unoxidized Organic (± 5%)	Sulfate (± 3%)
IL #6, Run 250, R1236	71	23	6
IL #6, Run 257, V1067	88	7	5
IL #6, Run 257, R1235	83	11	6
Wyodak, Run 258, R1235	99	0	1
Pitts., Run 259, R1235	78	16	6

Table 3. Relative percentages of the non-pyrrhotite sulfur in the resids determined by analysis of the pyrrhotite-subtracted sulfur XANES.

Sample	Sulfidic (±20%)	Thiophenic (±20%)	Sulfoxide (±20%)	Sulfone (±5%)	Sulfate (±10%)
IL#6, Run 250, R1236	13	78	2	0	7
IL#6, Run 257, V1067	21	28	17	2	32
IL#6, Run 257, R1235	21	38	15	3	23
Pitts., Run 259, R1235	0	81	3	0	15

Table 4. Mössbauer Parameters for Wilsonville Residues

SAMPLE	Phase	H(kG)	I.S.(mm/s)	Q.S.(mm/s)	%Fe
Run 258	Pyrrhotite	312	.75	-.07	34
R-1235	"	292	.73	.02	20
Wyodak	"	266	.70	.05	36
	Magnetite	468	.25		4
	Fe^{3+} silicate or Oxide	---	.40	1.07	6
Run 259	Pyrrhotite	311	.75	-.07	43
R-1235	"	289	.73	.01	25
Pitts.	"	264	.70	.06	27
	Fe^{3+} silicate or Oxide	---	.33	1.02	5
Run 250	Pyrrhotite	309	.76	-.06	36
R-1235	"	284	.73	.03	24
Ill #6	"	263	.70	.07	24
	Fe^{3+} sil./oxide	---	.31	1.01	9
	Fe^{2+} sulph.	---	1.22	2.61	7
Run 257	Pyrrhotite	311	.75	-.06	39
V-1067	"	289	.74	.02	17
Ill #6	"	266	.70	.06	28
	Fe^{3+} sil./oxide	---	.36	.90	9
	Fe^{2+} sulph.	---	1.18	2.68	7
Run 257	Pyrrhotite	311	.74	-.07	41
R-1235	"	287	.73	.03	21
Ill #6	"	264	.69	.06	24
	Fe^{3+} sil./oxide	---	.30	1.03	8
	Fe^{2+} sulph.	---	1.22	2.58	6

H is the magnetic hyperfine splitting in kGauss; I.S. is the isomer shift, relative to metallic iron, and Q.S. is the quadrupole splitting in mm/s. These parameters are used to identify the iron-bearing phase from the Mössbauer spectrum. %Fe is the percentage of iron present in a particular phase based on the relative areas under the peaks in the Mössbauer spectrum.

Table 5a. Derived Percentages for Forms of Sulfur in Argonne Premium Coals.

Sample	Wt% Total Sulfur	Sulfur forms, %					
		Pyrite	Sulfide	Thiophene	Sulfoxide	Sulfone	Sulfate
Pitts., PA	2.19	52	13	35	0	1	0
Illinois #6, IL	4.83	48	19	33	0	0	0
Wyodak-Anderson, WY	0.63	24	29	46	0	0	0

Table 5b. Mössbauer Data for Argonne Premium Coals.

Sample	Wt% pyritic sulfur	% Fe in		
		Clay	Siderite	Pyrite
Pittsburgh	1.26	1	0	99
Illinois	2.14	3	0	97
Wyodak	0.13	0	26	74
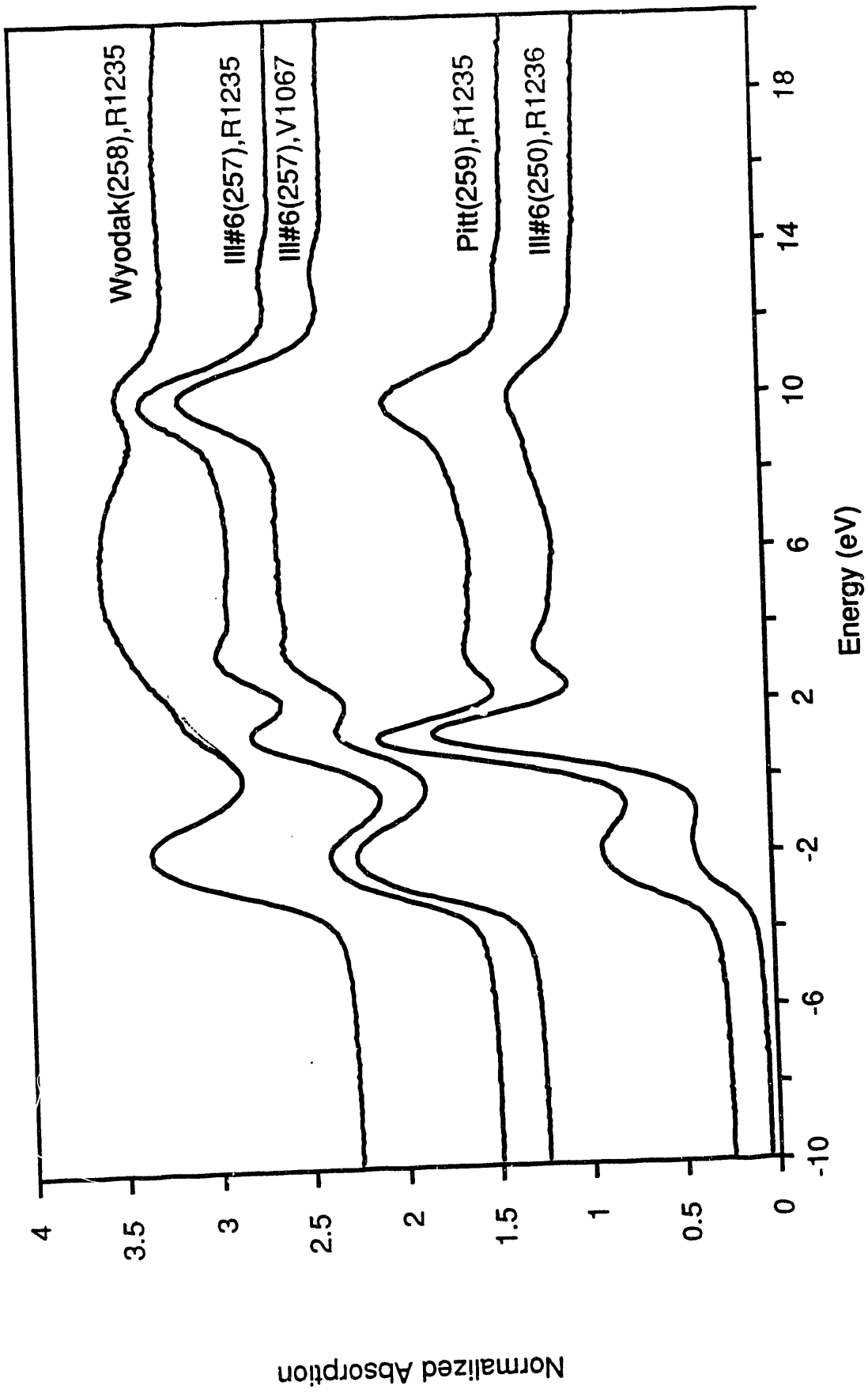
Figure 1. Sulfur XANES spectra obtained from five Wilsonville resid samples.

The plotted curves are labelled (top to bottom): Wyodak(258),R1235; III#6(257),R1235; III#6(257),V1067; Pitt(259),R1235; III#6(250),R1236.

X-axis: Energy (eV), ranging from -10 to 18.
Y-axis: Normalized Absorption, ranging from 0 to 4.

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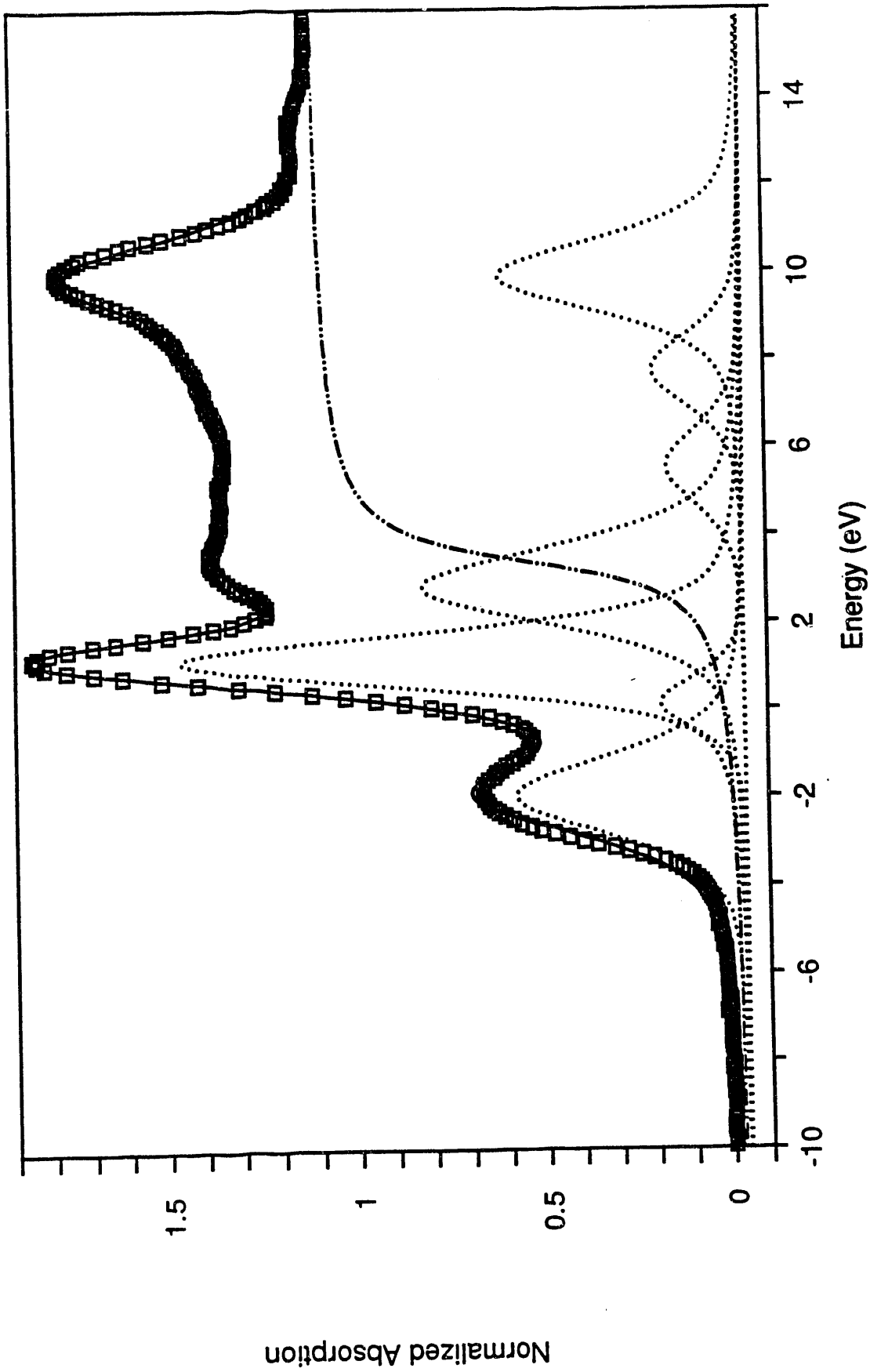
Figure 2. Fitted Sulfur XANES of interstage resid sample from Wilsonville run 259 of Pittsburgh coal (Ireland mine).
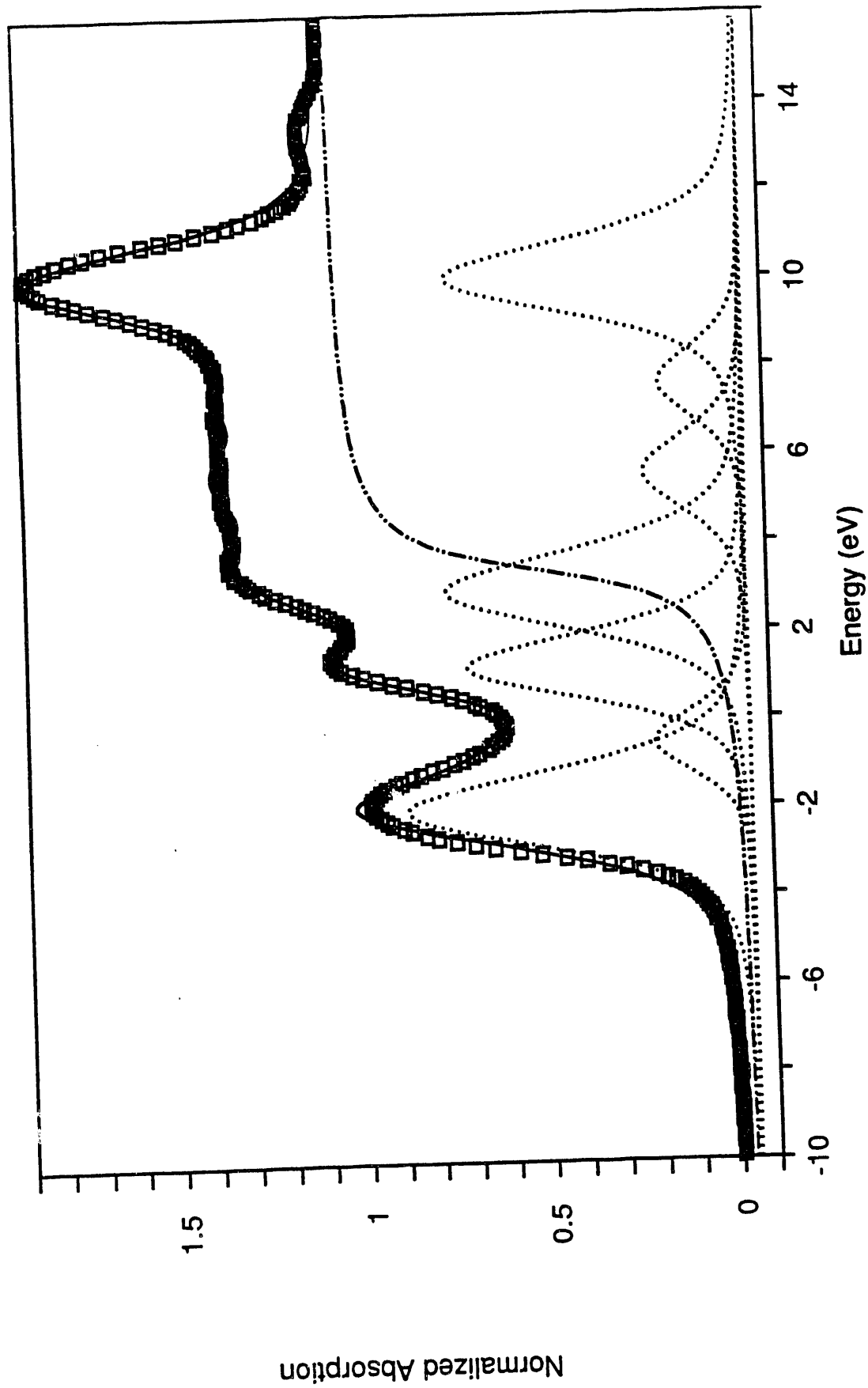
Figure 3. Fitted sulfur XANES of second stage product resid sample from Wilsonville Run 257 of Illinois #6 coal (Burning Star #2 Mine).

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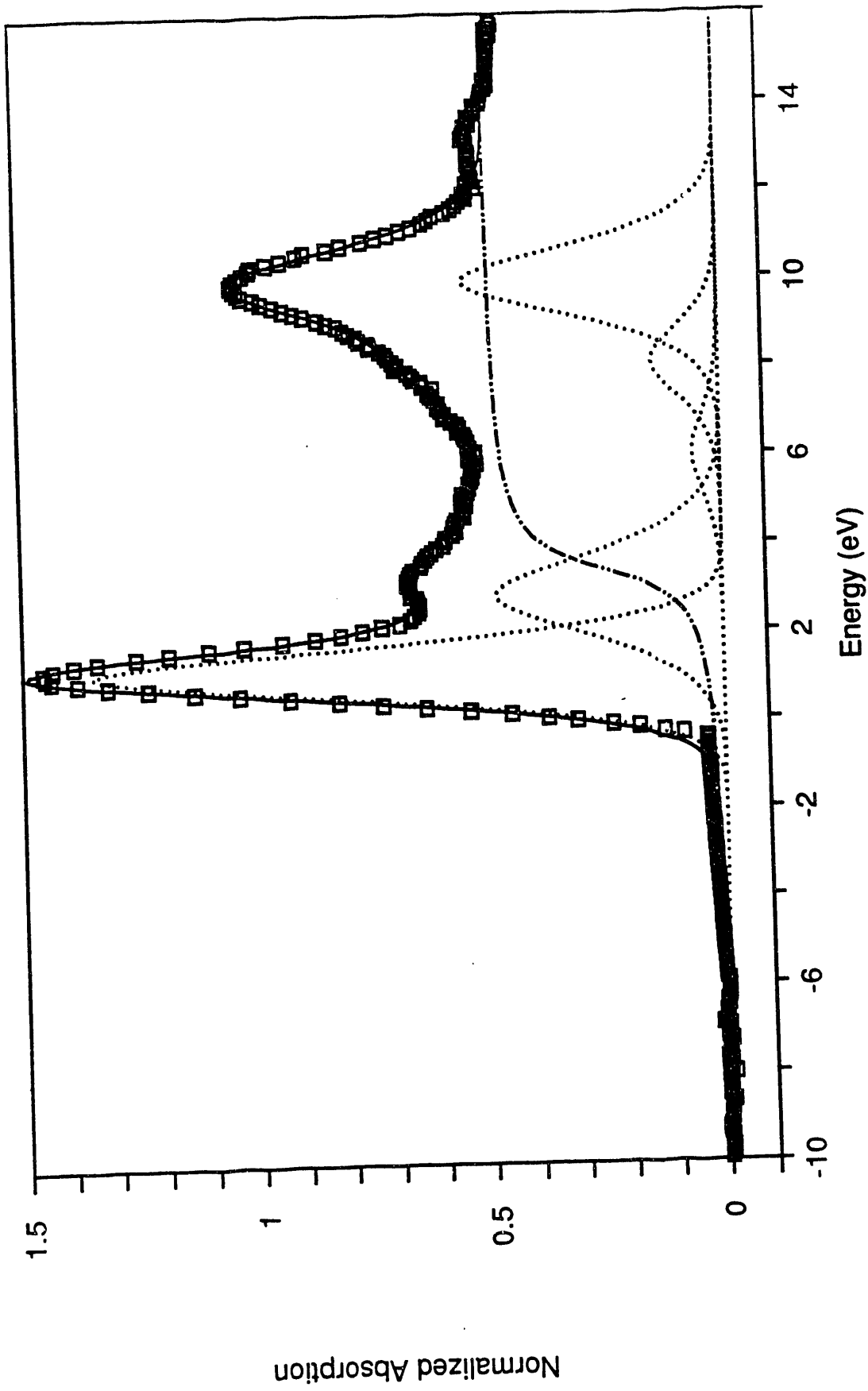
Figure 4. Fitted sulfur XANES of interstage resid sample subtracted with pyrrhotite XANES. Run 259, Pittsburgh (Ireland mine) coal.
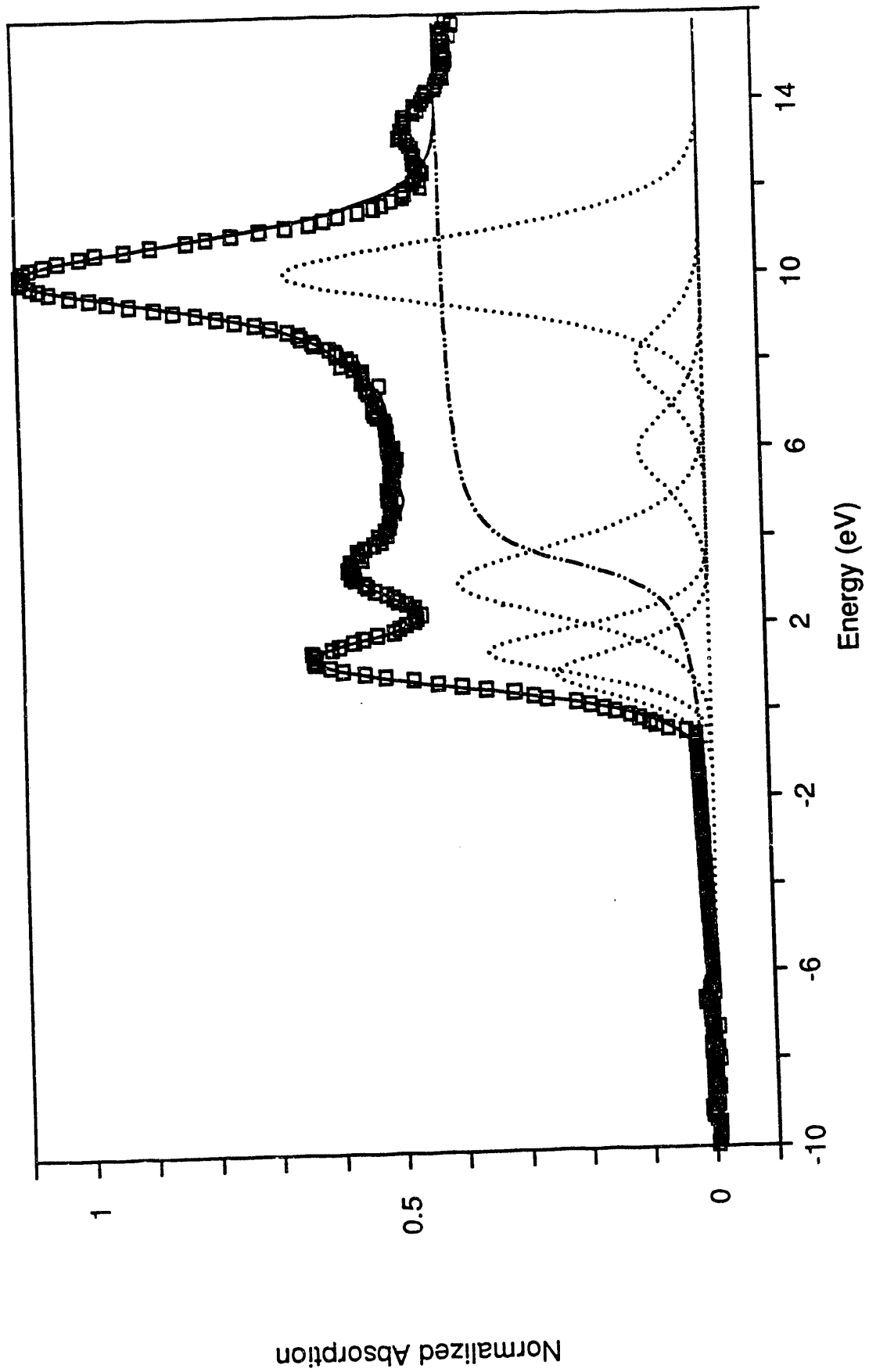
Figure 5. Fitted sulfur XANES of second stage product resid sample subtracted with pyrrhotite XANES. Run 257, Illinois #6 (burning star #2 mine) coal.

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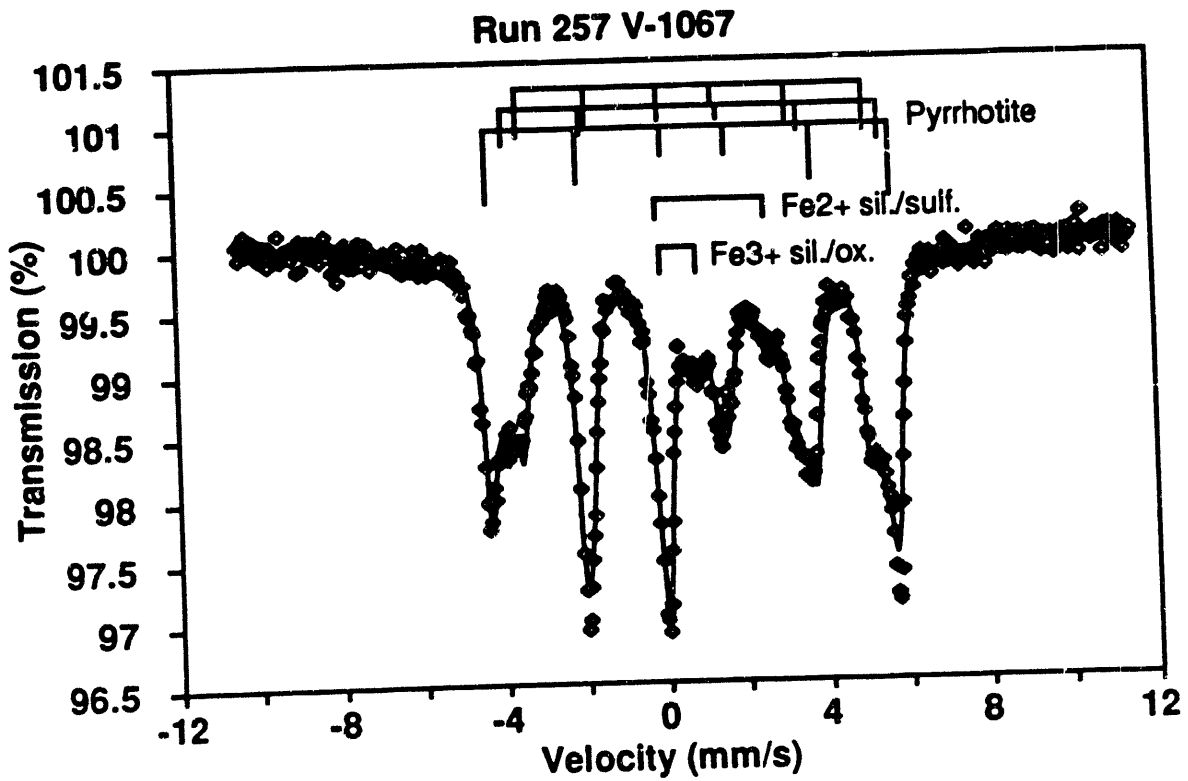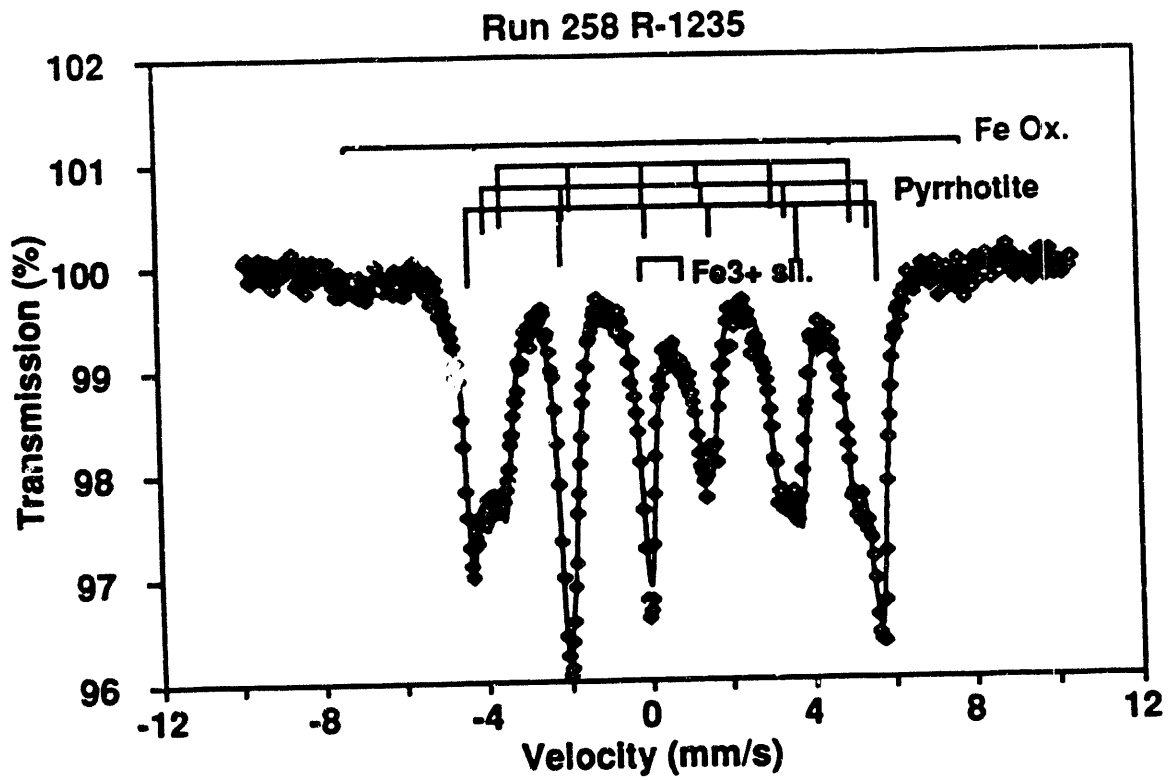
Figure 6. Typical Mossbauer spectra of Wilsonville Residues.

APPENDIX A

COMPILATION OF XAFS AND MÖSSBAUER SPECTRA
FOR WILSONVILLE RESID SAMPLES

1.   Compilation of least-squares fitted sulfur K-edge XANES spectra for all five Wilsonville resid samples investigated.

2.   Compilation of least-squares fitted sulfur K-edge XANES spectra with pyrrhotite spectral component subtracted for four Wilsonville resid samples investigated. [The fifth resid sample, Wyodak, was used as the pyrrhotite standard for the spectral subtraction, since ≈100% of the sulfur was present as this phase. Also see text.]

3.   Compilation of Mössbauer spectra for all five Wilsonville resid samples investigated.
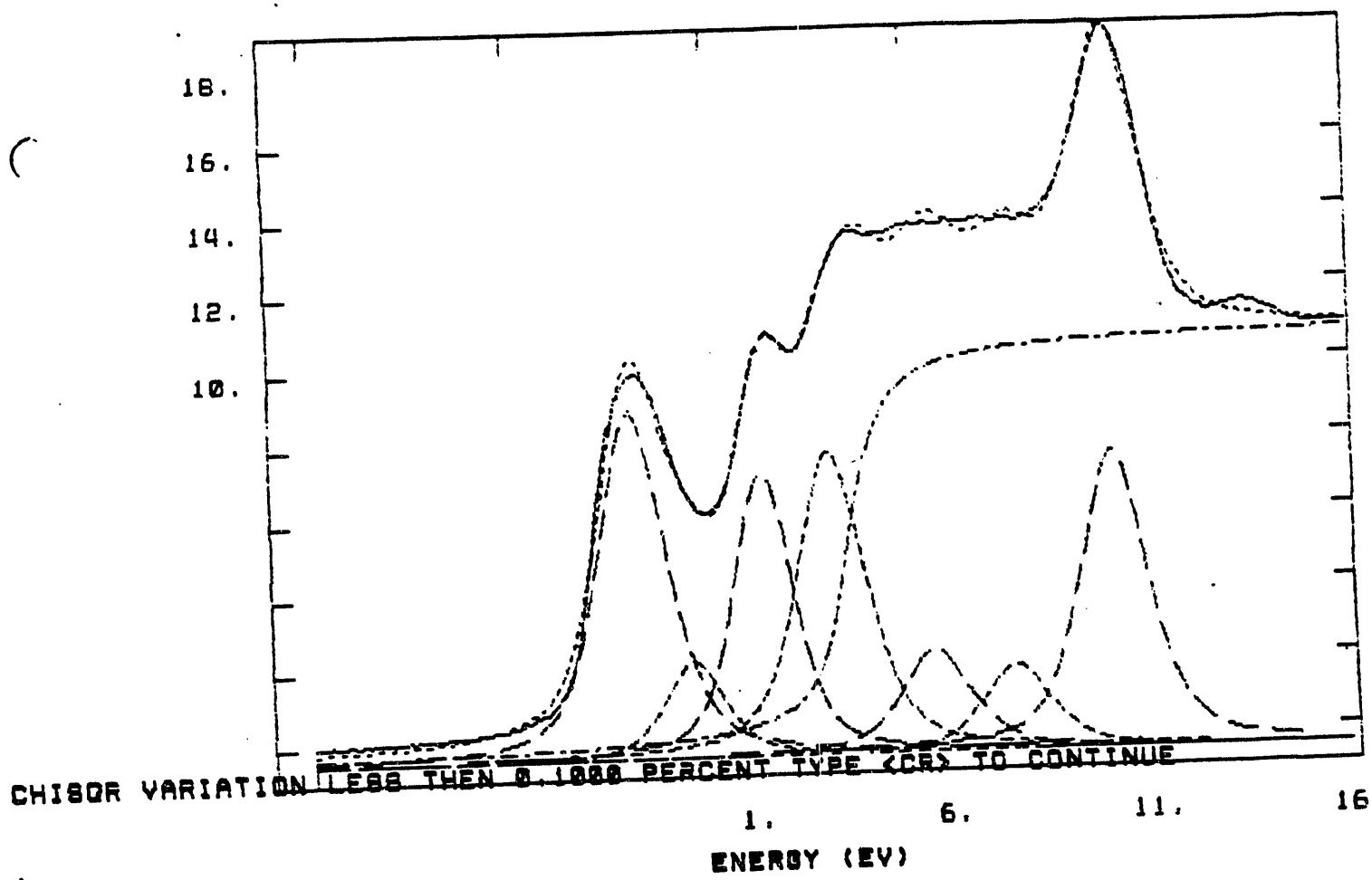
17

Al-1 Least-squares fitted sulfur XANES spectrum of Illinois #6 residue, R-1236, Run 250
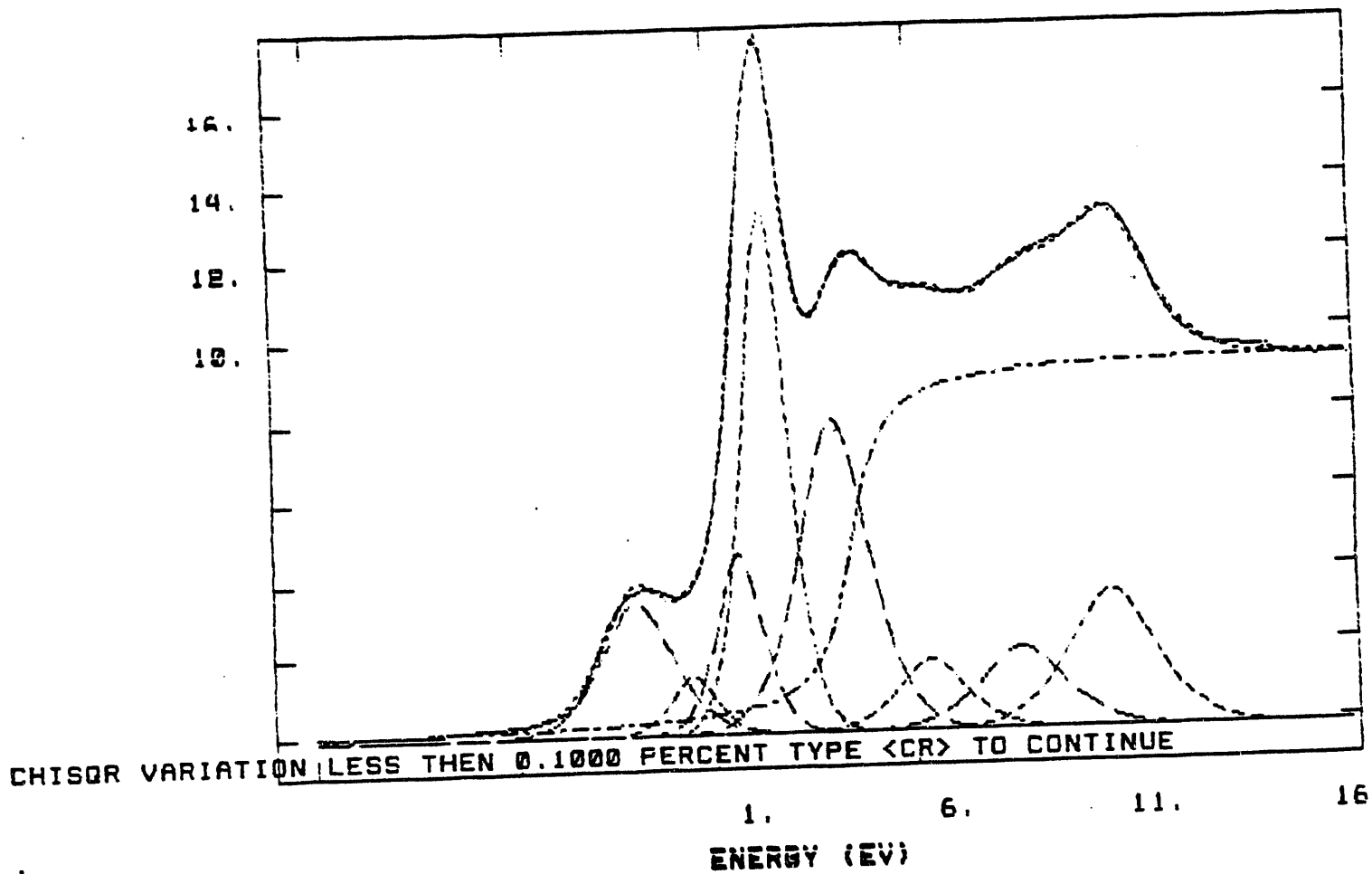
18

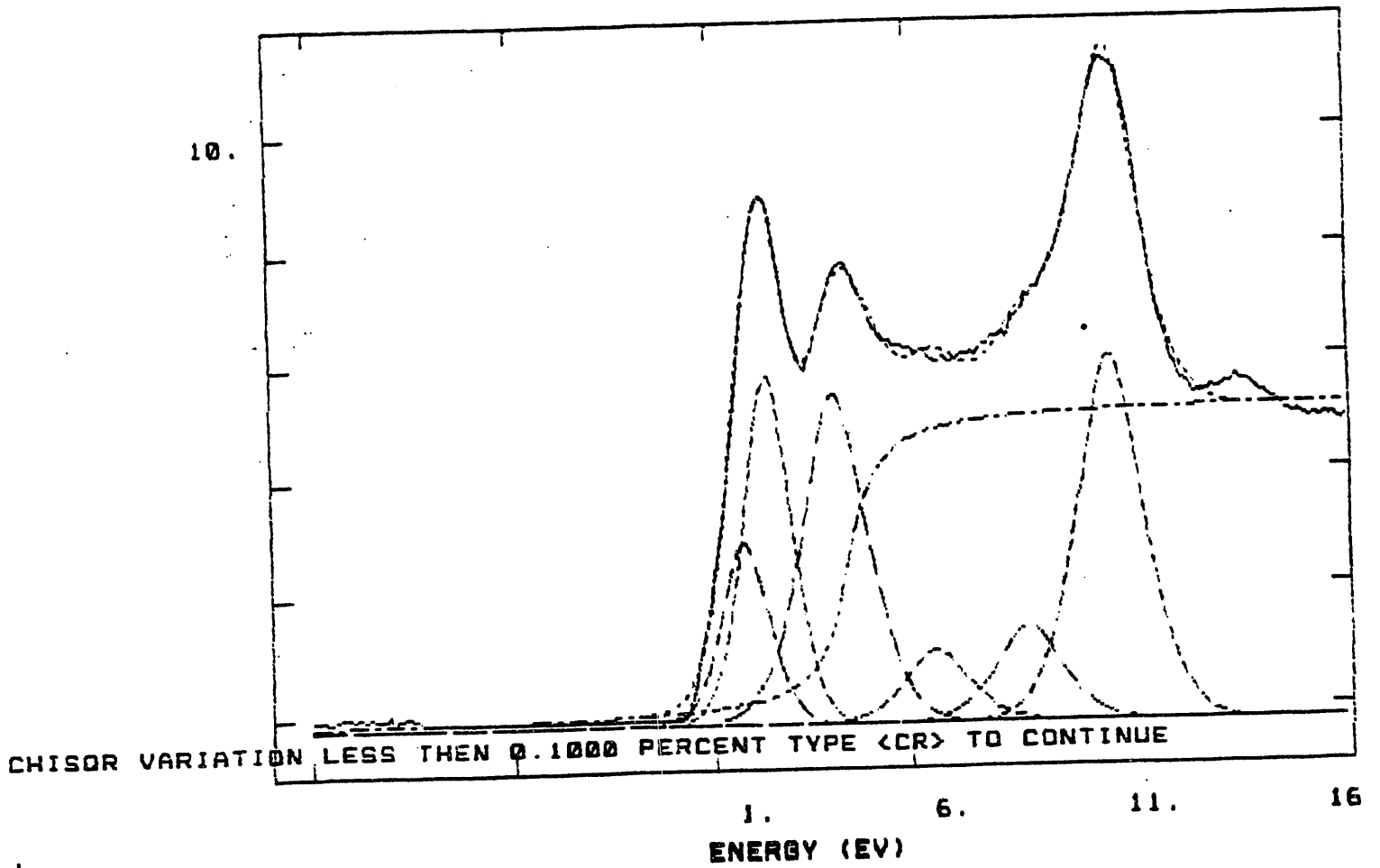Al-2 Least-squares fitted sulfur XANES spectrum of Illinois #6 residue, V-1067, Run 257
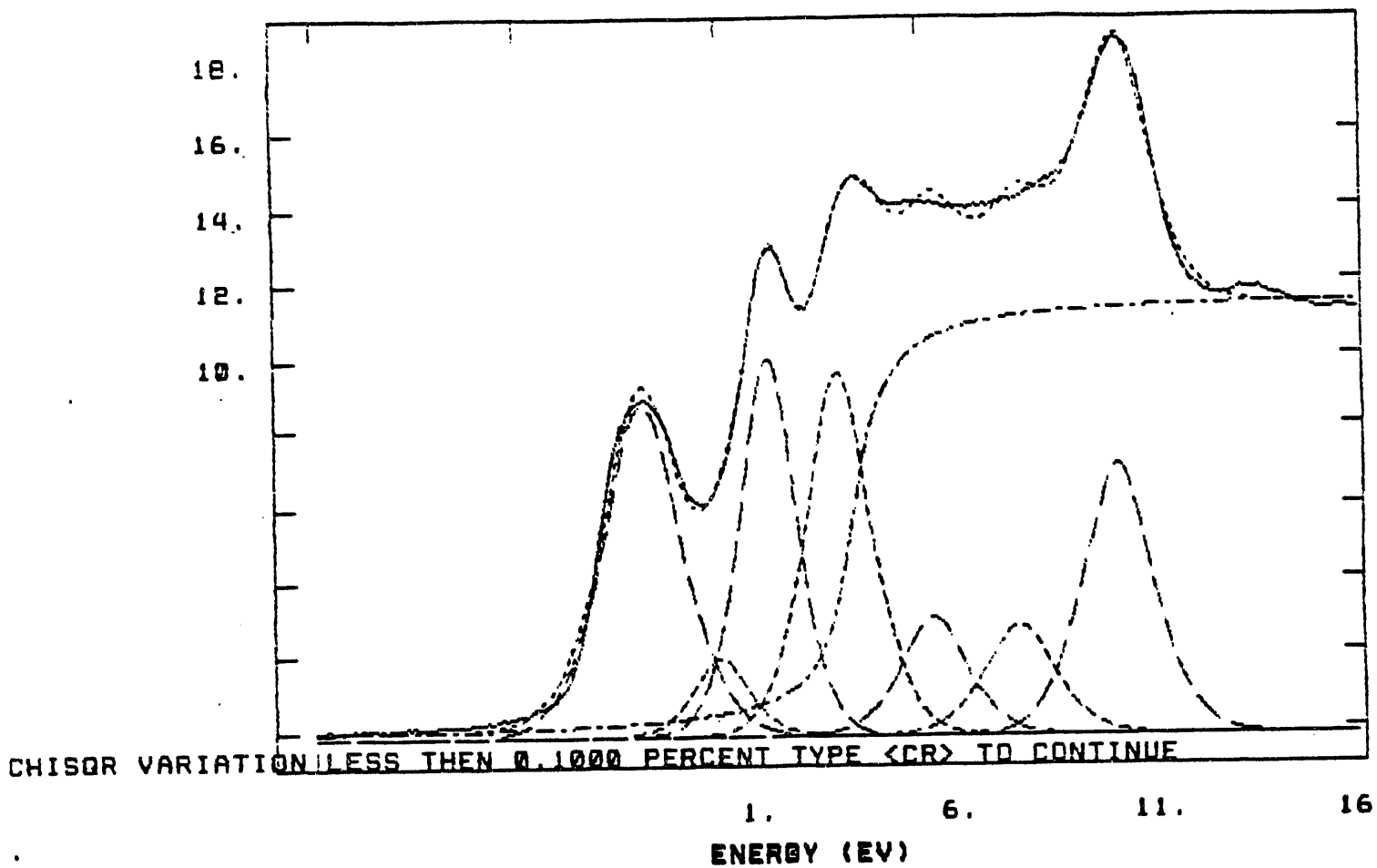
CHISQR VARIATION LESS THEN 0.1000 PERCENT TYPE <CR> TO CONTINUE

Al-3 Least-squares fitted sulfur XANES spectrum of Illinois #6 residue, R-1235, Run 257

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CHIOQR VARIATION LESS THEN 0.1000 PERCENT TYPE <CR> TO CONTINUE

ENERGY (EV)
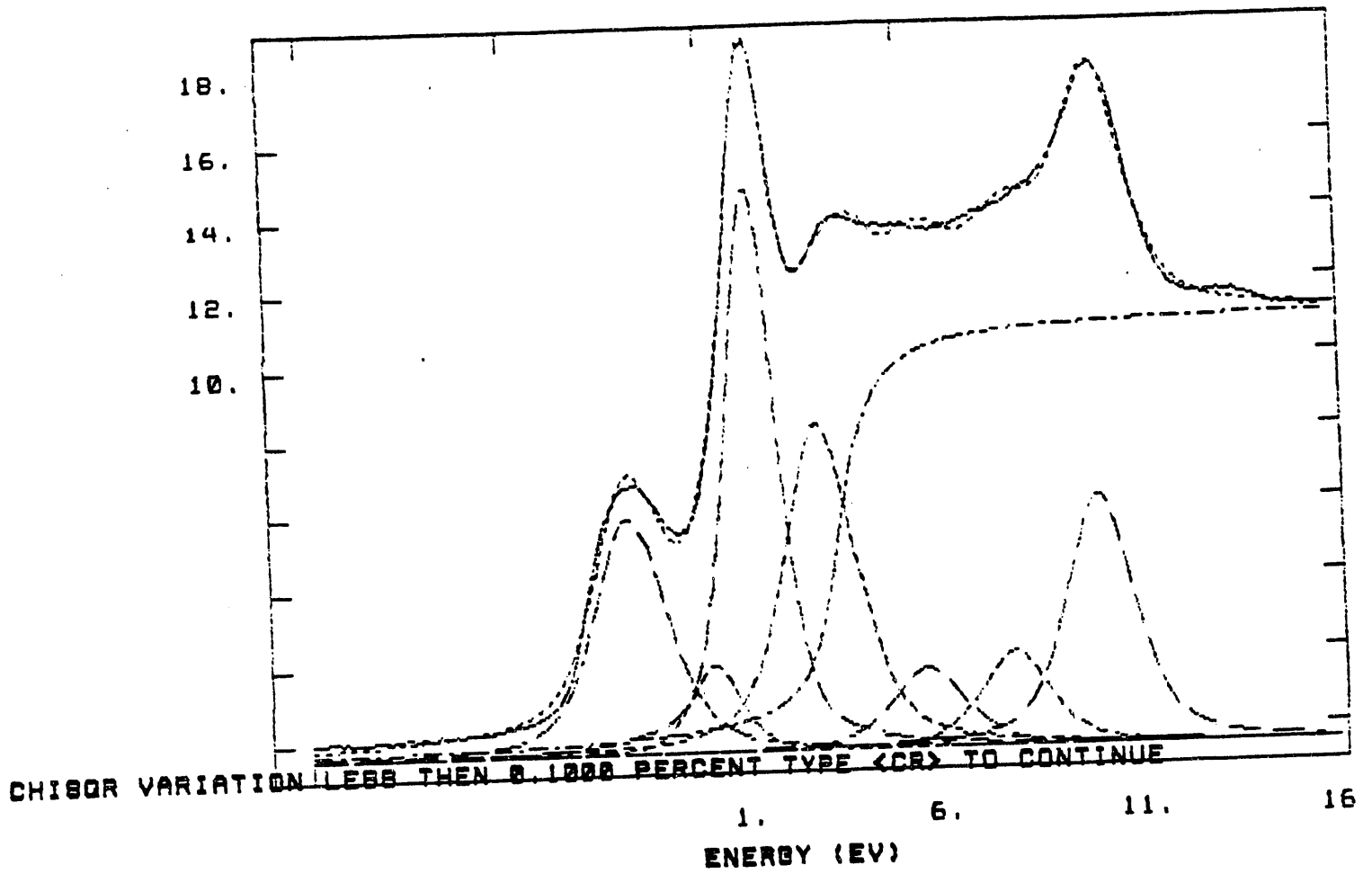
Al-4 Least-squares fitted sulfur XANES spectrum of Pittsburgh seam residue, R-1235, Run 259
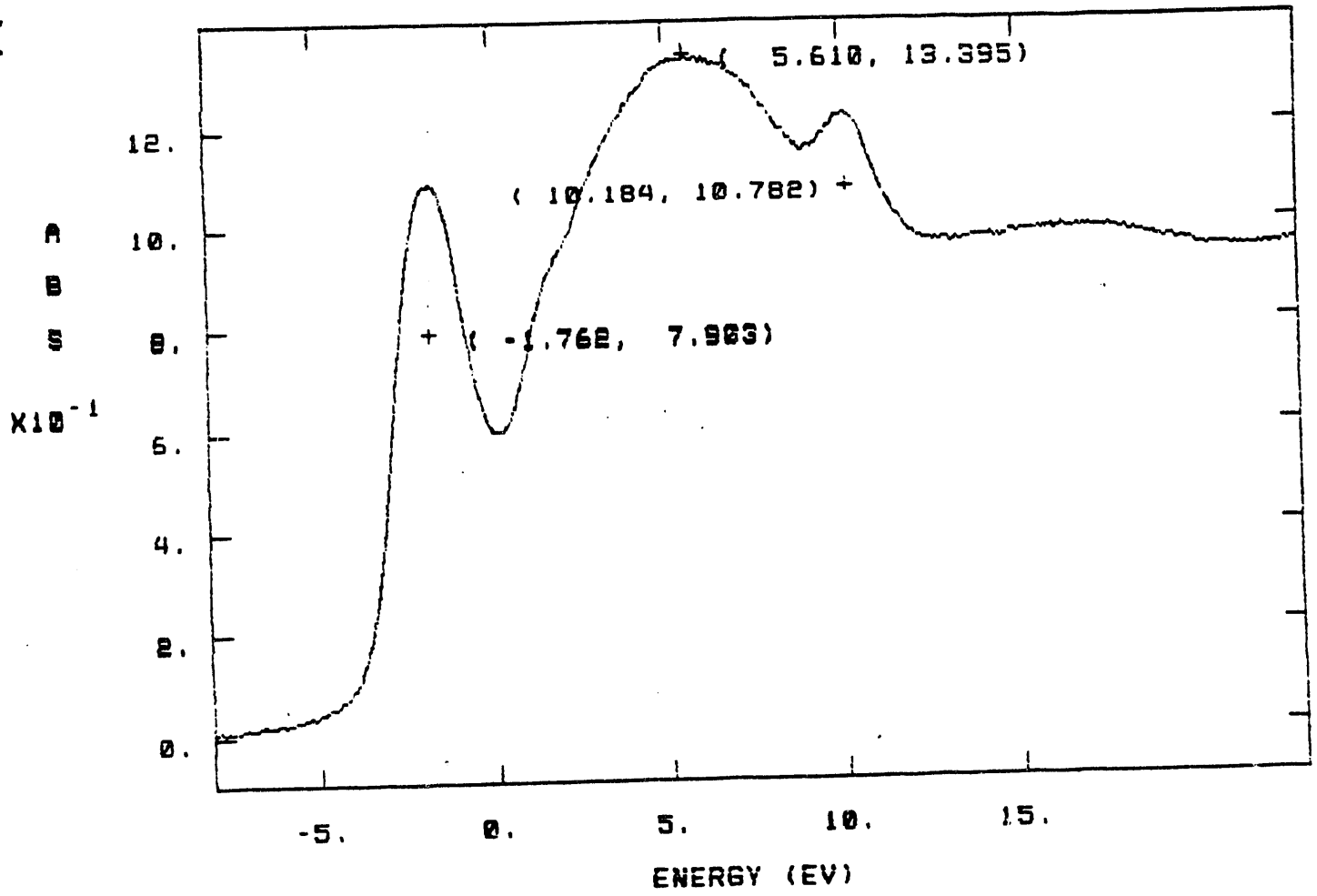
Al-5 Sulfur XANES spectrum of Wyodak residue, R-1235, Run 258

14.

12.

10.

CHISQR VARIATION LESS THEN 0.1000 PERCENT TYPE <CR> TO CONTINUE

1.   6.   11.

ENERGY (EV)
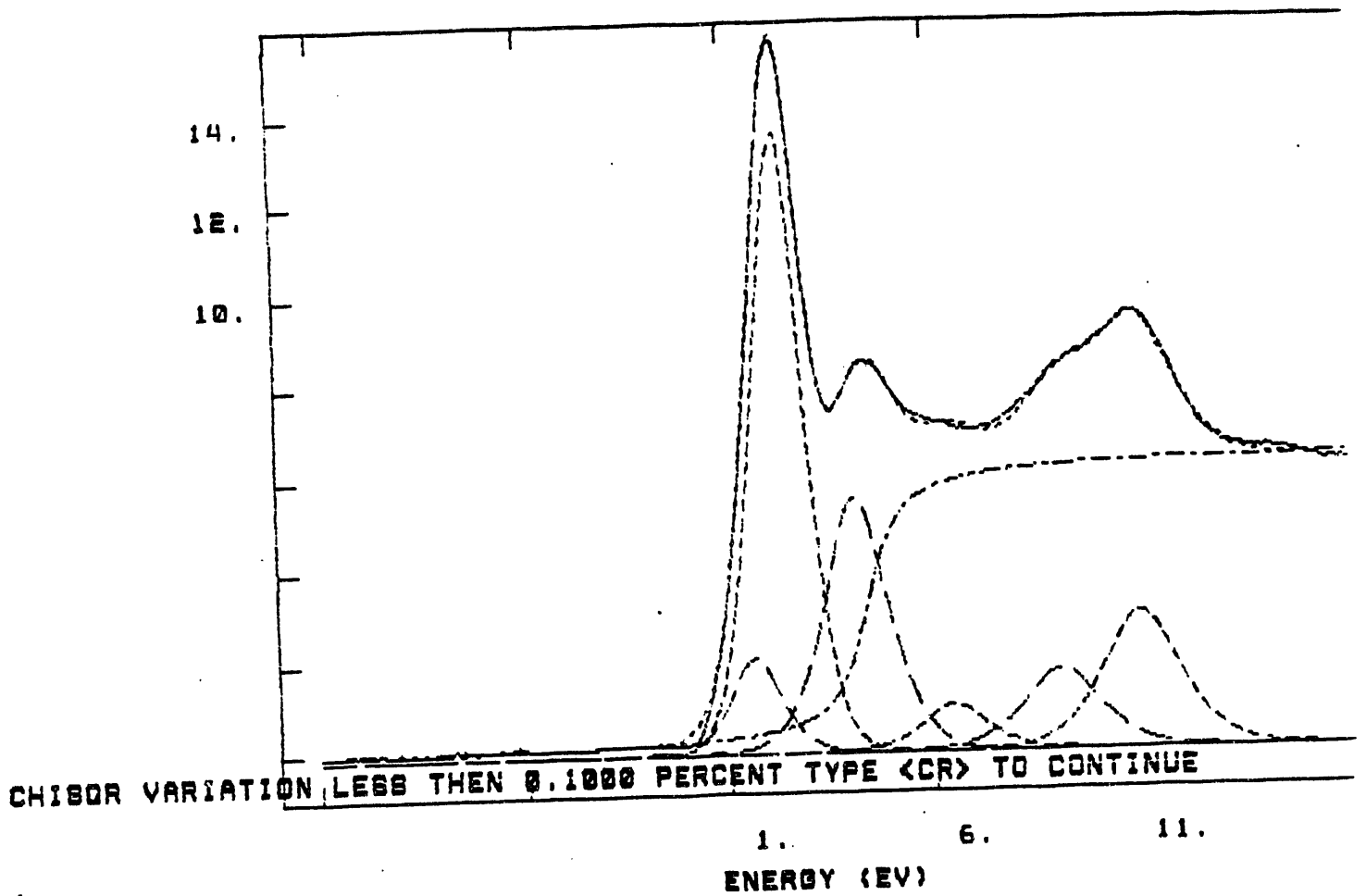
Figure A2-1 Least-squares fitted, pyrrhotite-subtracted, sulfur XANES spectrum of Illinois #6 residue, R-1236, Run 250

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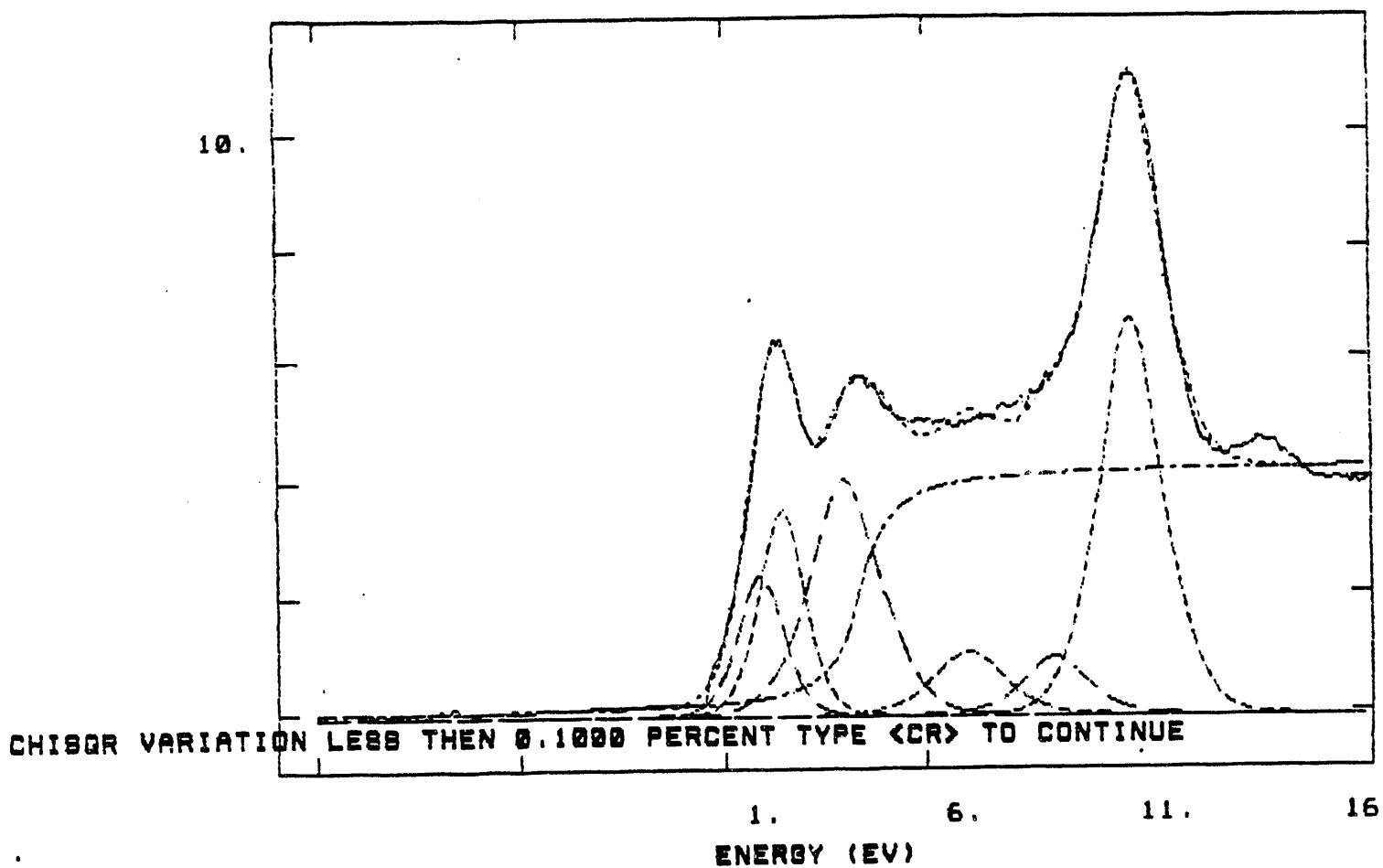
Figure A2-2 Least-squares fitted, pyrrhotite-subtracted, sulfur XANES spectrum of Illinois #6 residue, V-1067, Run 257
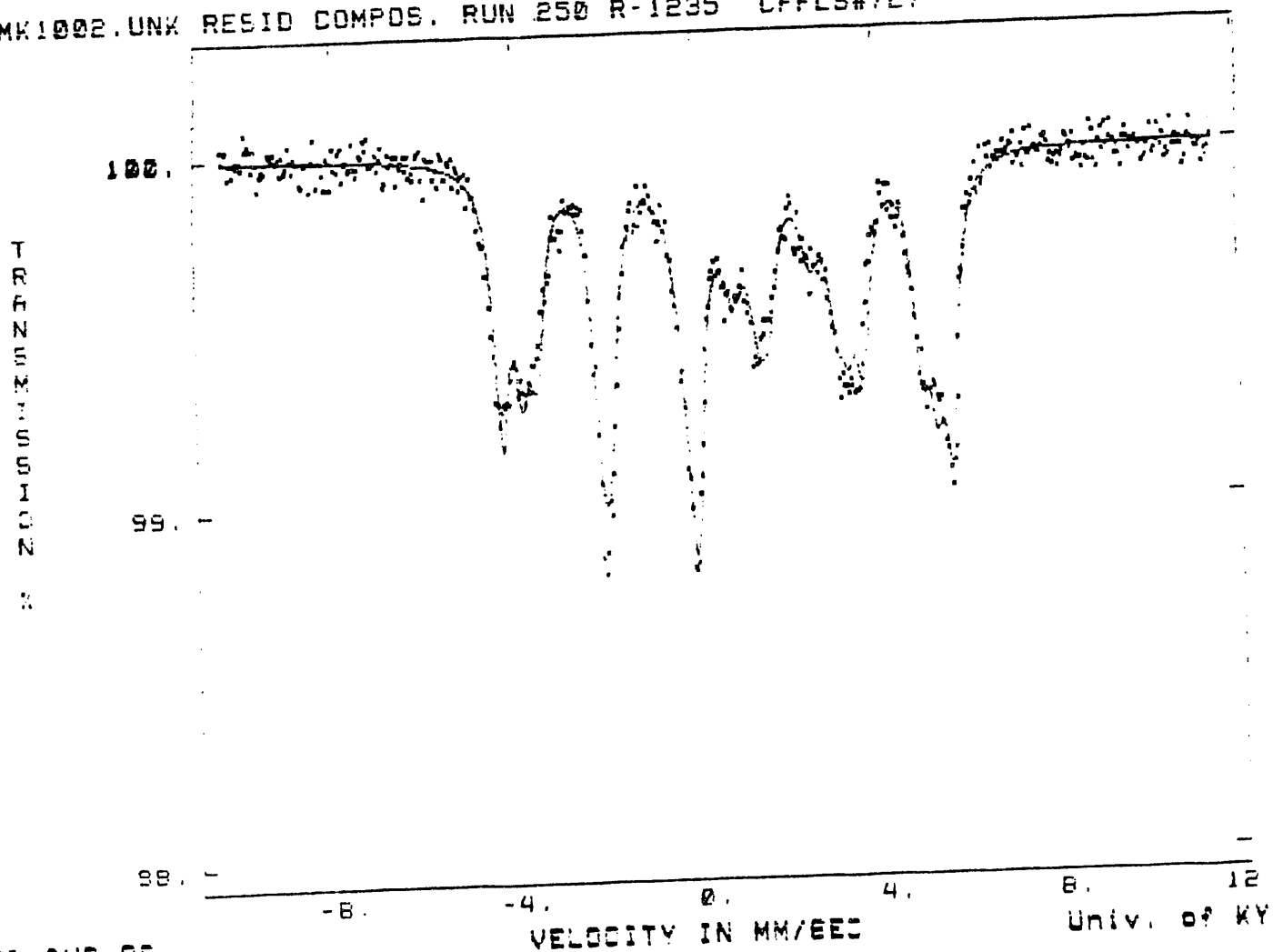
CHISOR VARIATION LESS THEN 0.1000 PERCENT TYPE <CR> TO CONTINUE

Figure A2-3 Least-squares fitted, pyrrhotite-subtracted, sulfur XANES spectrum of Illinois #6 residue, R-1235, Run 257
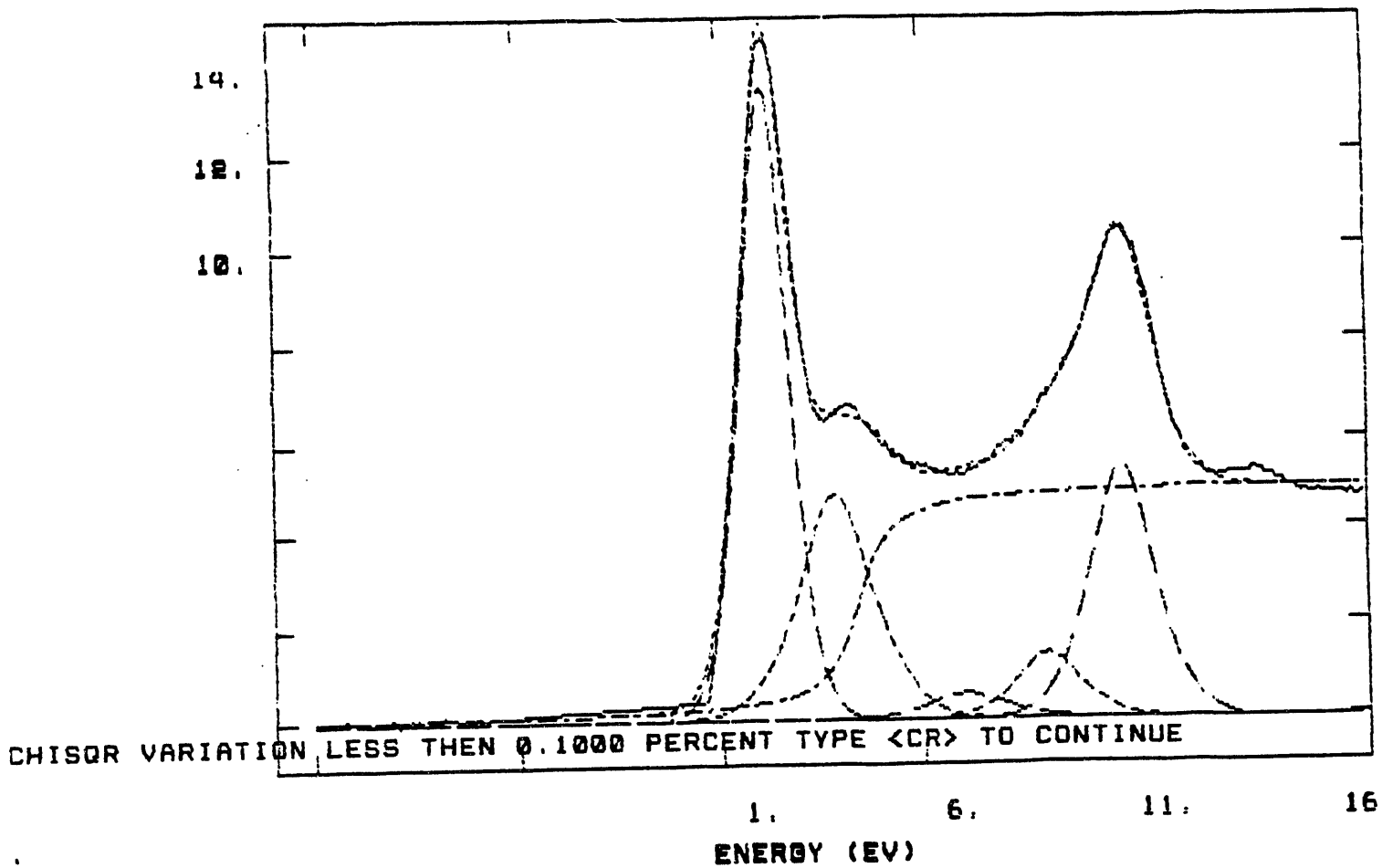
Figure A2-4 Least-squares fitted, pyrrhotite-subtracted, sulfur XANES spectrum of Pittsburgh seam residue, R-1235, Run 259

Figure A3-1: Mossbauer spectrum of Illinois #6 residue, R-1235, Run 250

Figure A3-2:   Mossbauer spectrum of Illinois #6 residue, V-1067, Run 257

"MK1003.UNK CONSOL RUN 257 V-1067   CFFL6#728

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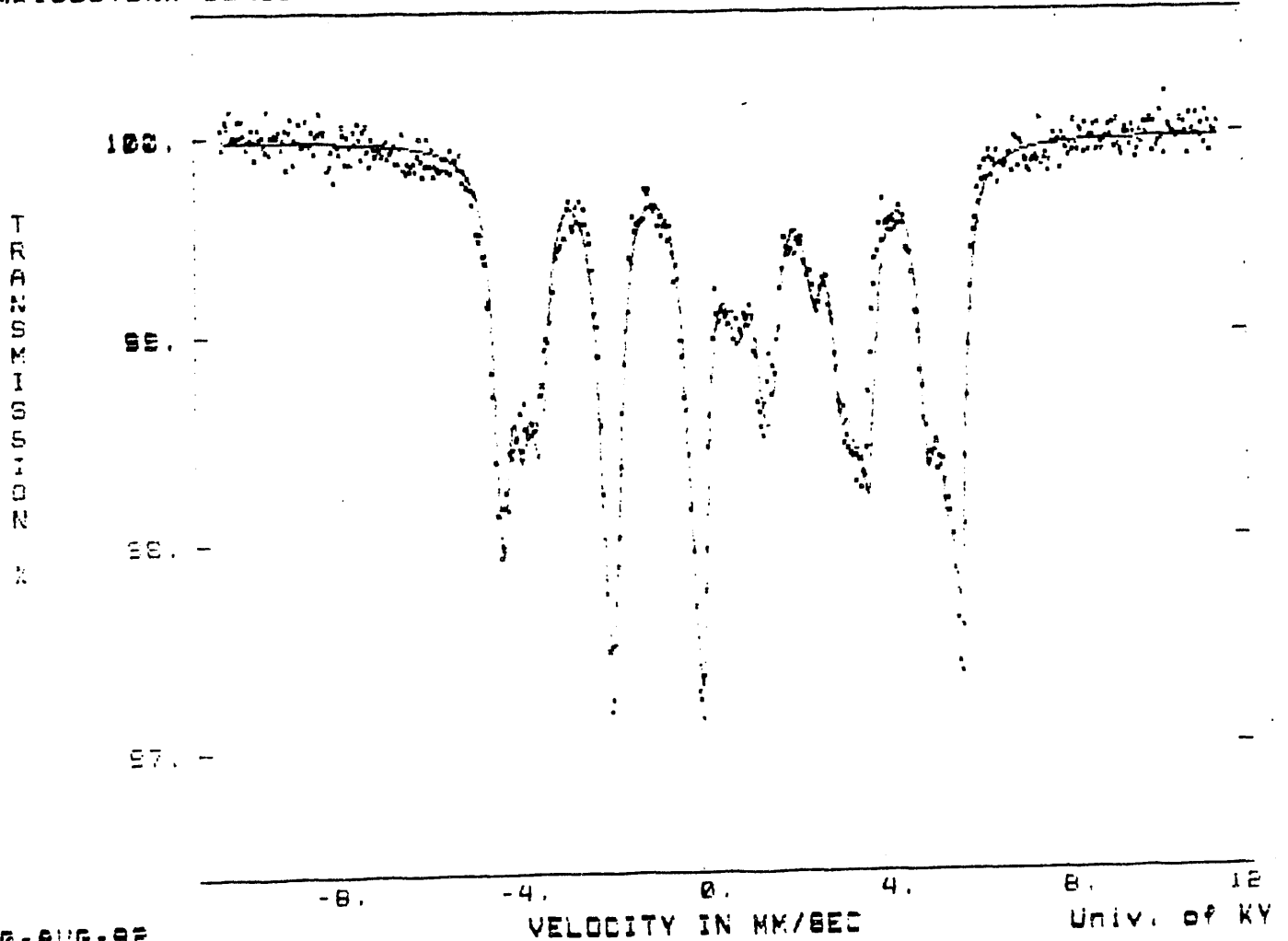
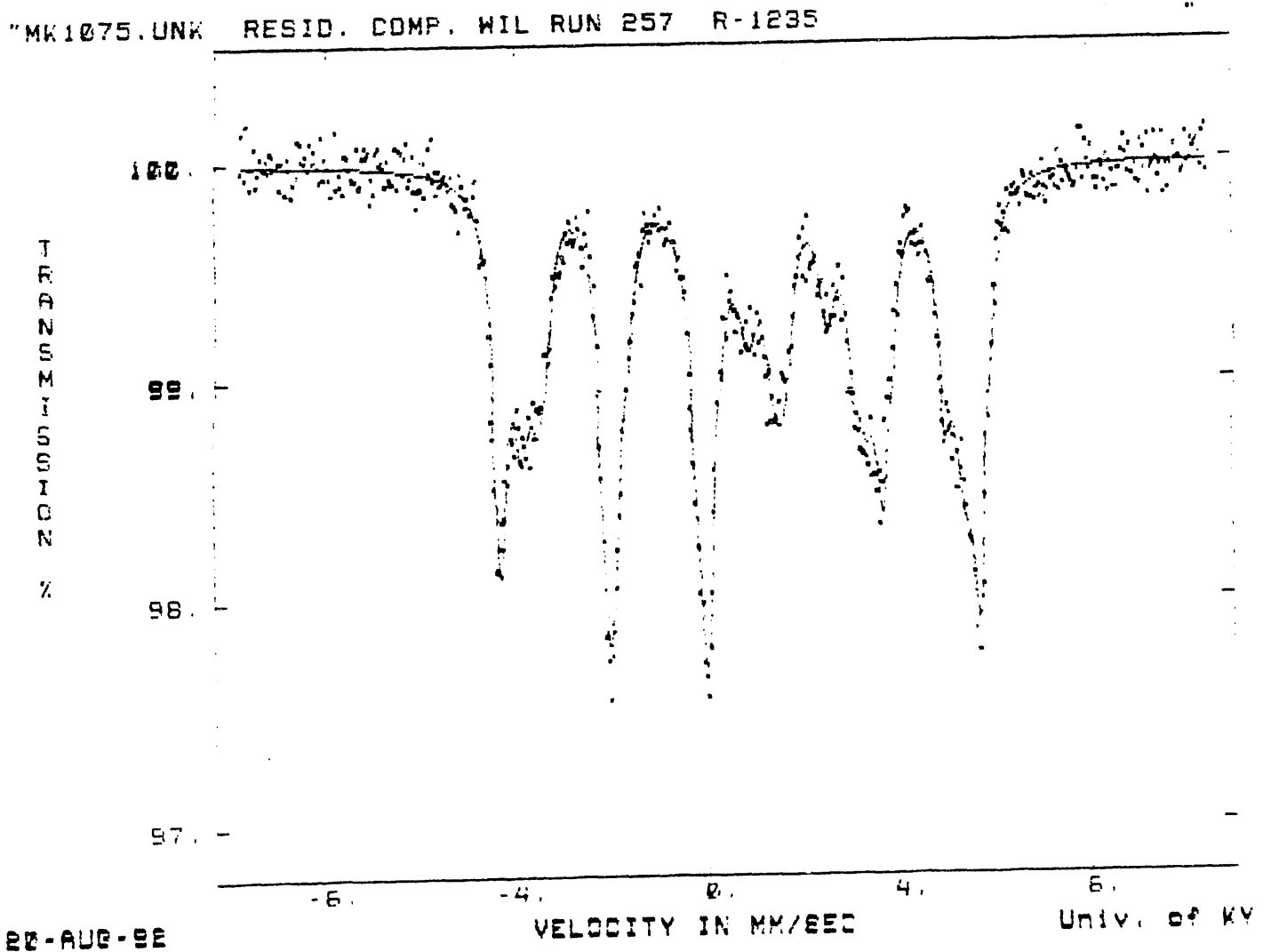Figure A3-3:   Mossbauer spectrum of Illinois #6 residue, R-1235, Run 257

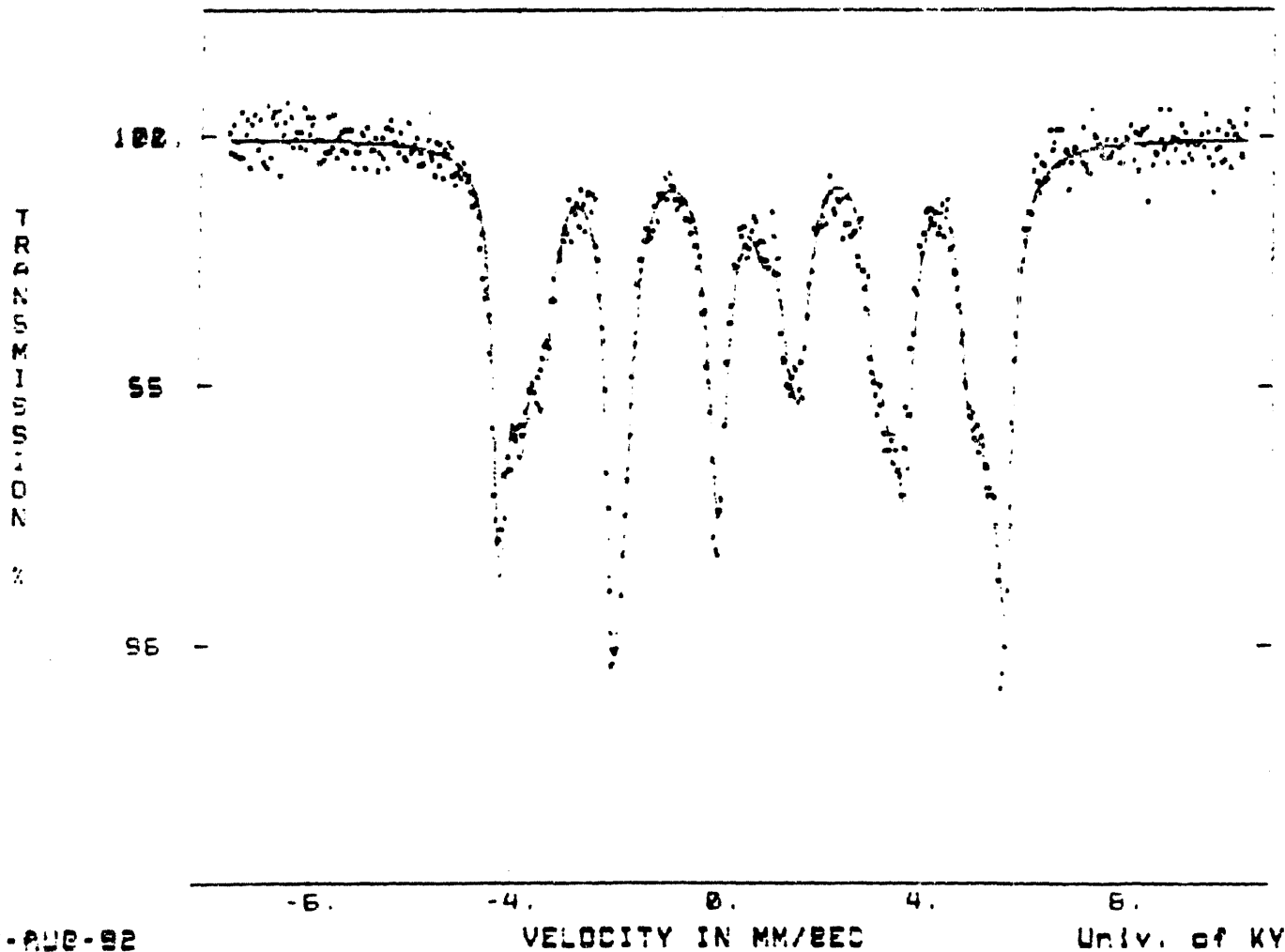"MK1075.UNK   RESID. COMP. WIL RUN 257   R-1235

Figure A3-4: Mossbauer spectrum of Pittsburgh seam residue, R-1235, Run 259
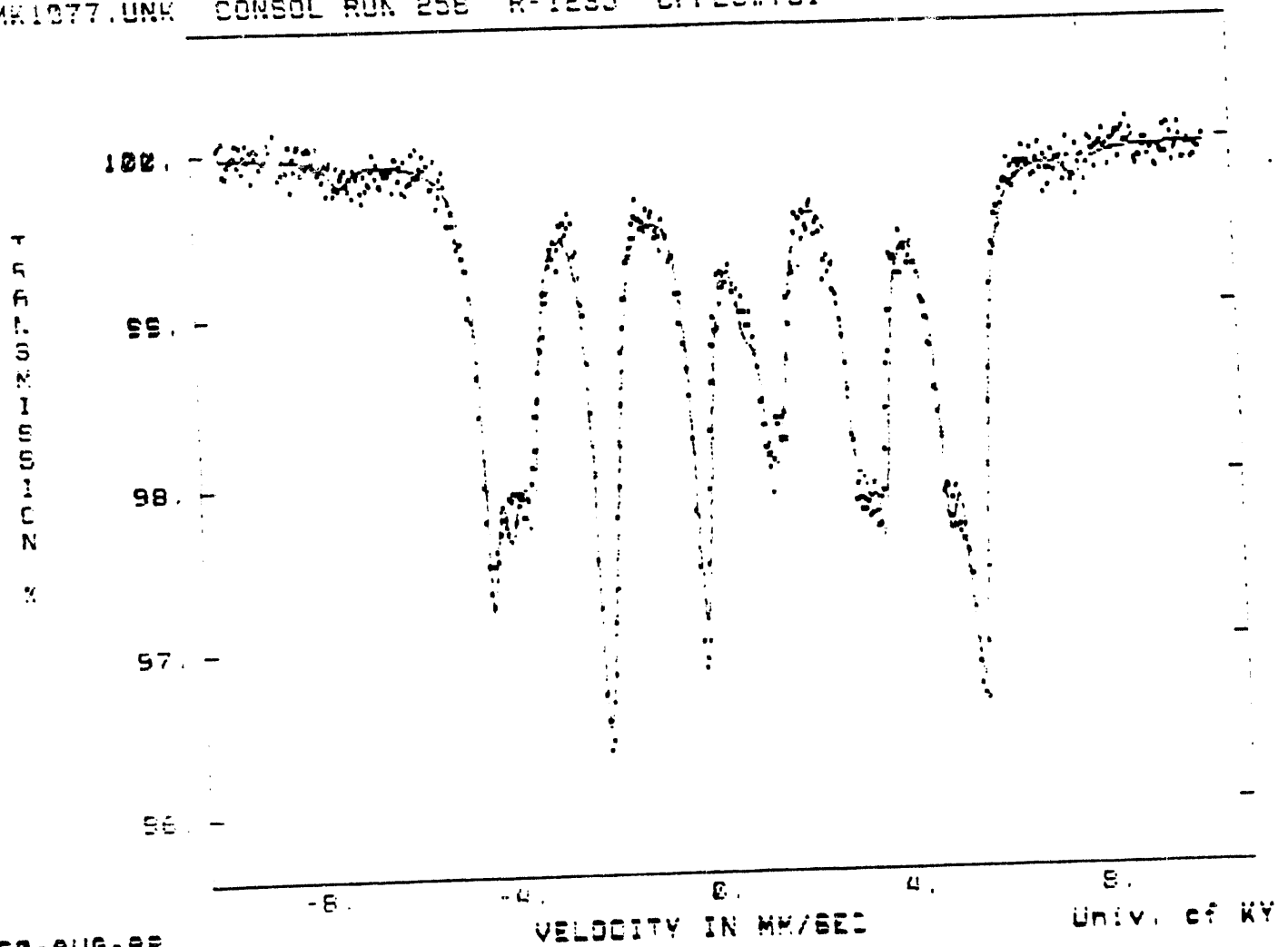

"MK1076.UNK Res. Comp. Run 259 r-1235   CFFLS #737

Figure A3-5: Mossbauer spectrum of Wyodak residue, R-1235, Run 258

"MK1077.UNK   CONSOL RUN 258   R-1235   CFFLS#731

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