

**NO DECOMPOSITION IN NON-REDUCING ATMOSPHERES**

Technical Progress Report for the Period  
September 1995-November 1995

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### SUMMARY OF TECHNICAL PROGRESS

New samples of Co(II)-ZSM-5 zeolites were prepared, and Co-containing ZSM-5 and erionite were studied *via* diffuse reflectant spectroscopy after being dehydrated at 350 and 500°C and after adsorption of carbon monoxide, water, and ethylene. In general, Co-ZSM-5 contains three different Co sites. However, Co-ZSM-5 prepared at acidic conditions contained only two different sites. One of these sites is probably identical with the Co site in Co-erionite. After dehydration at 500°C, Co siting in these zeolites was changed. In erionite at this same condition, Co ions were located in the plane of the single regular six-ring. Only strong ligands such as water could be adsorbed on Co ions in ZSM-5 zeolite dehydrated at 350°C, but Co ions in zeolites dehydrated at 500°C were also affected by weak ligands. Adsorption studies with NO are underway, and catalytic testing for NO decomposition and reduction over Co-containing zeolites will be carried out during the next quarter.

## TECHNICAL PROGRESS

The research during this quarter was centered on the study of Co siting in zeolites and on the detailed study of the interaction of the Co ions in various environments with guest molecules. Optical spectroscopy in the UV-VIS-NIR region at room and low (85K) temperature and adsorption of water, CO, and ethylene were used to investigate Co-containing ZSM-5 and erionite. Series of Co-ZSM-5 zeolites having different Co contents were prepared.

In general Co-ZSM-5 had a minimum of three cobalt sites with different environments. One site is characterized by the presence of a spectral band at  $15,000\text{ cm}^{-1}$ , and it is observed with samples prepared under basic conditions of ion exchange, preferentially in high silica ZSM-5. In Co-ZSM-5 samples exchanged at acid pH, there are present at least two other cobalt ion sites with different environments. These sites are characterized by 7-10 absorption bands. Co ions in these sites easily interact with strong guest molecules such as water.

After dehydration at  $500^{\circ}\text{C}$ , cobalt(II) ions in different environments are present in zeolites. These Co ions are also easily accessible to weak guest molecules such as CO and ethylene. Siting of all cobalt ions in ZSM-5 is different from the siting of Co(II) in A zeolite. Co erionite (dehydrated at  $350^{\circ}\text{C}$ ) exhibits a much simpler spectrum than Co-ZSM-5. Bands in the Co-erionite spectrum were also observed in the spectrum of Co-ZSM-5. Thus, there is at least one type of Co site common for both zeolites. Co(II) ions in this site in ZSM-5 zeolite were accessible only to strong guest molecules. The spectrum of Co-erionite dehydrated at  $500^{\circ}\text{C}$  is similar to the spectrum of Co-A zeolite, and this corresponds to Co ion with  $D_{3h}$  symmetry located in the plane of six-ring windows. Cobalt in this site

is easily accessible to guests molecules.

These studies provide input into the NO adsorption/desorption studies and NO catalytic decomposition/reduction studies over Co(II) zeolites that are being carried out. The results of those studies will be summarized in the next quarterly progress report.

## 1. EXPERIMENTAL

### 1.1. Ion Exchanged Samples

A series of Co(NH<sub>4</sub>)-ZSM-5 samples with a wide range of Co contents (0.25-2.6 wt%) was prepared under acidic conditions by ion exchange. Samples were prepared from NH<sub>4</sub>-ZSM-5 (Si/Al = 10) prepared at Air Products and Chemicals, Inc. by exchange from aqueous Co(NO<sub>3</sub>)<sub>2</sub> solutions with molarities of 0.01 or 0.02 at room temperature. The detailed conditions of the preparations are described in Table 1. The acid pH = 4.5 of the exchange solution was obtained by addition of 0.02 M HNO<sub>3</sub> to the mixture of 5 g zeolite with a corresponding amount of Co solution. The pH = 4.5 represents the natural pH of a mixture of 1 g of zeolite with 8.5 ml 0.01 M solution of Co(NO<sub>3</sub>)<sub>2</sub>. Samples 40, 44, and 45 were prepared by double or triple exchange treatments, and values in Table 1 represent the condition of each step of the preparation. At the end of each step of exchange, the zeolite mixture was filtered and new Co solution was added. All samples were filtered, washed with 1000 ml of distilled water, and dried at 110°C.

**TABLE 1.** Conditions of preparation and resultant Co(II) content of Co(NH<sub>4</sub>)-ZSM-5 zeolites prepared under acidic conditions of ion exchange.

| Sample Number | Co Content in Zeolite (wt%) | Conditions of Preparation              |                      |            |                          |
|---------------|-----------------------------|--|----------------------|------------|--------------------------|
|               |                             | Vol. of exchange solution/g of zeolite | Time of exchange (h) | Initial pH | Co exchange solution (M) |
| 35            | 1.65                        | 135                                    | 2                    | 4.50       | 0.01                     |
| 36            | 0.3                         | 8.5                                    | 2                    | 4.51       | 0.01                     |
| 37            | 0.8                         | 25.5                                   | 2                    | 4.22       | 0.01                     |
| 38            | 1.7                         | 76.5                                   | 2                    | 4.50       | 0.01                     |
| 39            | 2.3                         | 272                                    | 3                    | 4.15       | 0.01                     |
|               |                             | 272                                    | 3                    | 4.42       | 0.01                     |
| 40            | 2.4                         | 400                                    | 2                    | 4.50       | 0.01                     |
|               |                             | 400                                    | 3                    | 4.50       | 0.01                     |
|               |                             | 400                                    | 3                    | 4.52       | 0.01                     |
| 41            | 0.25                        | 3.6                                    | 2                    | 4.33       | 0.01                     |
| 42            | 1.25                        | 36                                     | 3                    | 4.40       | 0.01                     |
| 43            | 1.8                         | 16                                     | 2                    | 4.47       | 0.01                     |
| 44            | 1.6                         | 76                                     | 2                    | 4.54       | 0.01                     |
|               |                             | 26                                     | 2                    | 4.55       | 0.01                     |
| 45            | 2.6                         | 76                                     | 2                    | 4.49       | 0.01                     |
|               |                             | 800                                    | 12                   | 4.52       | 0.02                     |
|               |                             | 800                                    | 12                   | 4.52       | 0.02                     |

The Co concentration in each zeolite was estimated *via* DRS spectroscopy. The integrated intensity of the VIS absorption band of fully hydrated Co-ZSM-5 was compared with a calibration curve (Co-ZSM-5: Si/Al = 10, Co 4.4 wt%; Co-ZSM-5: Si/Al = 22.5, Co 0.75 wt%; Co-erionite: Si/Al = 3.5, Co 3.2 wt%, where these Co-containing zeolites are described in [1]). This method of estimating the Co(II) content in prepared samples was

used due to the small amount of zeolites prepared, and most of the samples shall be chemically analyzed later. Co-ZSM-5 samples previously prepared [1,2] are summarized in Table 2.

**TABLE 2.** Co-ZSM-5 zeolites prepared at different conditions.

| Sample Number | Zeolite                    | Co Concentration (wt%) | Si/Al Ratio |
|---------------|----------------------------|------------------------|-------------|
| 28            | Co(NH <sub>4</sub> )-ZSM-5 | 4.4                    | 10          |
| 29            | Co(NH <sub>4</sub> )-ZSM-5 | 4.0                    | 10          |
| 30            | Co(NH <sub>4</sub> )-ZSM-5 | 2.0                    | 10          |
| 31            | CoNa-ZSM-5                 | 4.0                    | 10          |
| 32            | Co(NH <sub>4</sub> )-ZSM-5 | 0.5                    | 10          |
| 33            | CoNa-ZSM-5                 | 0.6                    | 10          |
| 34            | CoNa-ZSM-5                 | 0.6                    | 22.5        |

## 1.2. DRS Spectroscopy

Procedures used for the optical measurements at room temperature were described earlier [1,2]. Spectra were evaluated by the Schuster-Kubelka-Munk theory;  $F(R) = (1-R)^2/(2R)$ . Samples were dehydrated at 350°C as described earlier [1]. Co-erionite, Co-ZSM-5/45, and Co(NH<sub>4</sub>)-ZSM-5/28 zeolites, where /xx indicates the sample number given in Table 1 or Table 2, were dehydrated at temperatures ranging from 400 to 550°C. In these cases, the zeolite was first dehydrated at 350°C as described in [1], and after this it was dehydrated at higher temperature from 1 to 12 h.

An additional experiment was carried out in which Co(NH<sub>4</sub>)-ZSM-5/29 was dehydrated for 1 h in a stream of helium at 515°C. The zeolite was first evacuated at room temperature for 30 min, and then under evacuation it was heated at a rate of 5°C/min to



515°C. This treatment corresponds to the procedure of sample calcination before testing catalytic activity.

### 1.2.1. DRS at Low Temperature

The UV-VIS spectrum of Co(NH<sub>4</sub>)-ZSM-5/29 was recorded at low temperature. A quartz cuvette with evacuated double front window and with a through-flow jacket cooled by a flow of liquid nitrogen was used for this measurement. A flow of dry gaseous nitrogen, 20 ℓ/min was maintained through the analysis chamber of the spectrometer in which the temperature of the sample cell was 85K.

### 1.2.2. Adsorption and Desorption of CO, H<sub>2</sub>O, and C<sub>2</sub>H<sub>4</sub>

Adsorption and desorption of CO and H<sub>2</sub>O with Co(NH<sub>4</sub>)-ZSM-5 and Co-erionite samples were studied in detail *via* UV-VIS-NIR DRS spectroscopy. After the zeolite was dehydrated at 350 or 550°C, the amount of gas adsorbed by *ca.* 0.8 g of dry sample was regulated by adsorption of gas at pressures of 0.5-700 (NO, CO) or 0.5-22 Torr from 40, 180, and 1400 ml volumes at atmospheric pressure. Carbon monoxide (99.0+%, Aldrich Chemical Company, Inc.) was purified by freezing liquid nitrogen and then thawing. After adsorption at room temperature, desorption of gas was studied at temperatures ranging from room temperature to 440°C. Samples were evacuated from 30 min to 3 h.

## 2. RESULTS

### 2.1. Co-ZSM-5 Dehydrated at 350°C

#### 2.1.1. Concentration Dependence of UV-VIS DR Spectra

Spectra of Co-ZSM-5 samples with Co contents from 0.25 to 2.6 wt% exhibits two maxima in the 12,000-30,000 cm<sup>-1</sup> spectral region. The first maximum (A) was at about

17,000 and the second maximum (B) was located at approximately 20,000  $\text{cm}^{-1}$  (Figures 1 and 2). Upon normalization of the spectra, little difference connected with concentration changes was observed (Figure 3). The dependence of the area of VIS absorption band of the dehydrated samples as a function of Co concentration is given in Figure 4. This dependence is nonlinear and indicates the presence of at least one more spectroscopical compound in the spectra of the more highly exchanged samples of  $\text{Co}(\text{NH}_4)\text{-ZSM-5}$ . Existence of more components in the spectra is also confirmed by the linear decrease of the position of band B located at  $\approx 20,000 \text{ cm}^{-1}$  with increasing  $\text{Co}(\text{II})$  concentration (Figure 5).

The dependence of the ratio of maximum intensity of the 20,000  $\text{cm}^{-1}$  spectral band (B) to maximum intensity of the 17,000  $\text{cm}^{-1}$  spectral band (A) on the  $\text{Co}(\text{II})$  concentration is shown in Figure 6. This concentration dependence exhibiting a linear increase with increasing concentration is characteristic for two different sites, one of which is occupied preferentially at low concentration, but its occupation is saturated at high concentration. It can be concluded that  $\text{Co}(\text{NH}_4)\text{-ZSM-5}$  zeolite contains  $\text{Co}(\text{II})$  ions in a minimum of two different sites.

### 2.1.2. Detail Analysis of VIS Spectrum of $\text{Co}(\text{NH}_4)\text{-ZSM-5}$

In the VIS spectra of  $\text{Co}(\text{NH}_4)\text{-ZSM-5}$  zeolites two main optical bands were present as described above, but the irregularities in features of these spectra indicate the presence of several overlapping bands. To distinguish these individual bands and to approximately determine the maxima of these bands in wavenumbers, the second derivative mode of these spectra was determined. The validity of this method was confirmed by comparison of second derivative mode of fully hydrated  $\text{Co-ZSM-5}$  containing 1.65 wt%  $\text{Co}(\text{II})$  (Figure 7). All bands corresponding to transitions of complexes of octahedral cobalt(II) observed in the

VIS region at room temperature (cf. ref. 3) were found and no artificial spectral band was observed here.

Second derivatives plots of the VIS band of  $\text{Co}(\text{NH}_4)$ -ZSM-5 zeolites dehydrated to  $350^\circ\text{C}$  are shown in Figure 8. It is possible to identify absorption bands with minima around 15,900, 17,000, 17,400, 17,800, 18,350, 19,500, 20,000, and 21,000  $\text{cm}^{-1}$ . The presence of this large number of individual spectra features in spectra of Co-ZSM-5 zeolites was confirmed by recording the spectrum of Co-ZSM-5 38 (Co 1.7 wt%) dehydrated at  $350^\circ\text{C}$  at temperature of 85K. This spectrum is shown in Figure 9, and its second derivative mode with calculated data prints is shown in Figure 10. Eight bands with minima corresponding approximately to the minima recorded at room temperature (Figure 8) are observed in this spectrum. Moreover, three additional bands are evidenced using this second derivative mode. Bands with minima near 15,500, 16,500, and 22,300  $\text{cm}^{-1}$  are not clearly evident in the spectra recorded at room temperature. It is evident that this large number of apparent spectral features cannot be attributed to Co ions in different lattice sites in the ZSM-5 zeolite without further experiments. Although the VIS spectrum of  $\text{Co}(\text{NH}_4)$ -ZSM-5 zeolite dehydrated at  $350^\circ\text{C}$  is composed from many overlapping bands (at approximately 15,500, 15,900, 16,500, 17,000, 17,400, 17,800, 18,350, 19,500, 20,000, 21,000, and 22,300  $\text{cm}^{-1}$ ) these bands probably correspond to Co(II) ions in only two or three different environments.

### 2.1.3. Adsorption of CO and $\text{H}_2\text{O}$

Adsorption studies were carried out using CO at pressures of 20, 100 (180 ml) and 600 Torr (1400 ml) over Co-ZSM-5/45 dehydrated at  $350^\circ\text{C}$ . There was no significant effect of CO adsorption on the Co(II) spectrum, as is shown in Figure 11. This result agrees with the observation that the only decrease of pressure of CO corresponded to expansion of CO

to the volume of the spectroscopic cell.

In contrast, adsorption of water affected the Co(II) spectrum in the zeolite dehydrated at 350°C, as shown in Figures 12 and 13. The effect was observed for adsorption of a small amount of water (22 Torr, 180 ml), as well as in the presence of excess water. Upon water adsorption, the intensity of the Co absorption bands decreased, and there were also observable changes in the spectrum shape. The decrease of intensity of absorption in the VIS region and absence of a symmetrical triplet centered around 17,000  $\text{cm}^{-1}$  indicate that a tetrahedral cobalt(II) complex was not present in the partially hydrated Co-ZSM-5 zeolite. This is in agreement with observations of sample dehydration when the high intensity blue band (typical for tetrahedral coordinated cobalt) was not observed in any stage of sample dehydration.

Adsorption of water, along with the absence of adsorption of CO, on the Co(II) ions indicate that most of the Co(II) ions are located in sites accessible only to strong ligands (i.e.  $\text{H}_2\text{O}$ ) but not to weak ligands (CO). The absence of CO adsorption can be explained by blocking of the Co(II) ion by a stronger guest molecule (possibly an OH group).

## 2.2. Co-ZSM-5 Dehydrated at Higher Temperatures

### 2.2.1. VIS Spectrum of Dehydrated Co-ZSM-5

Samples of Co-ZSM-5/30 and Co-ZSM-5/45 were dehydrated for 4 h at 510°C and 12 h at 525°C. There were dramatic changes in the Co spectrum, as is shown in Figures 14 and 15. Absorption bands characteristic for dehydrated Co-ZSM-5 disappeared and new bands with low intensity appeared, consisting of a complex band centered at 17,500  $\text{cm}^{-1}$  (composed from bands at 16,000, 17,000 and 19,000-20,000  $\text{cm}^{-1}$ ), a single weak band at 22,200  $\text{cm}^{-1}$ , and a band centered at 24,800  $\text{cm}^{-1}$ . The differences in appearance of the two

spectra shown in Figure 14 indicate that the spectrum of Co-ZSM-5 dehydrated at 500°C represents more Co(II) in more sites. A distinct band at 22,500 cm<sup>-1</sup> was not observed in these cobalt containing zeolites.

The band at ≈25,000 cm<sup>-1</sup> might be a doublet that would be similar to the doublet observed for dehydrated Co-A zeolite. This doublet was identified as <sup>4</sup>E'' → <sup>4</sup>E'' transitions of Co(II) ion in an environment with D<sub>3h</sub> symmetry localized in the trigonal oxygen plane of the regular six-ring window of A-zeolite [4]. There is no evidence for the presence of regular six-ring windows in the ZSM-5 framework. Explanation of this spectrum requires further experiments and computations of term diagrams of cobalt(II) ions in crystal fields with various low symmetries.

### 2.2.2. Adsorption of CO and H<sub>2</sub>O

The effect on the spectrum of exposure of CO to the Co-ZSM-5/45 zeolite dehydrated at 525°C is shown in Figure 16, and it seems that CO strongly affected the cobalt(II) spectrum. Bands at 22,200 and 24,800 cm<sup>-1</sup> disappeared, the complex band consisting of at least a triple in the 15,500-18,000 cm<sup>-1</sup> region was broadened into a more distinct asymmetric triplet (probably quartet) with bands at 16,000, 18,000, (19,500) and 21,000 cm<sup>-1</sup>. These dramatic changes indicate that Co ions in the ZSM-5 matrix dehydrated at 500°C were easily accessible to guest molecules.

The spectrum of Co-ZSM-5/45 with adsorbed water is given in Figure 18. As in the case of CO adsorption, the spectrum of cobalt(II) in dehydrated zeolite was strongly affected by adsorption of water molecules. As shown in Figure 19, bands at 22,200 and 24,800 cm<sup>-1</sup> disappeared and the triplet at about 17,000 cm<sup>-1</sup> was increased in intensity and the higher wavenumber component was shifted from ≈18,000 cm<sup>-1</sup> to ≈19,800 cm<sup>-1</sup>. The spectrum

exhibited features of the spectrum of Co-ZSM-5 dehydrated at 350°C and of the band at  $\approx 17,000 \text{ cm}^{-1}$  of Co-ZSM-5/45 dehydrated at 525°C. It indicates that after adsorption of water, the Co sites corresponding to the zeolite dehydrated at 350°C are restored, but this needs further confirmation.

### 2.2.3. Adsorption of Ethylene

Ethylene at pressures of 0.5 Torr (40 ml), 0.95 Torr (180 ml) and 450 Torr (1400ml) was adsorbed onto Co-ZSM-5/30 (preparation of sample is described in Section 2.2.1.), resulting in spectra that are shown in Figures 20 and 21. The band centered at  $22,500 \text{ cm}^{-1}$  was most sensitive to adsorption of the guest molecule and disappeared at low pressure of ethylene. At high pressure of ethylene, the band at  $\approx 25,000 \text{ cm}^{-1}$  also disappeared and the broad band centered at  $\approx 17,500 \text{ cm}^{-1}$  increased in intensity and split into a distinct symmetric triplet with maxima at 15,100, 16,900, and  $18,750 \text{ cm}^{-1}$ .

The ethylene-Co(II)A zeolite complex was studied by Klier et al. [5], and an asymmetric triplet was reported to be characteristic for ethylene adsorbed on cobalt(II) in a regular six-ring window. A symmetric triplet for a ethylene-Co-ZSM-5 complex does not correspond to this report. Moreover, the observed spectrum of Co-ZSM-5 with adsorbed ethylene was distinctly different from the spectrum of the ethylene-CoA complex. The symmetrical triplet shown in Figure 21 for this ethylene-Co-ZSM-5 complex indicates that Co(II) ions are not located in regular six-rings and that the absorption band at  $25,000 \text{ cm}^{-1}$  in the spectrum of dehydrated Co-ZSM-5 corresponds to symmetry different from  $D_{3h}$  symmetry.

## 2.3. Co-ZSM-5 Dehydrated Under Various Conditions

### 2.3.1. Co-ZSM-5 Dehydrated in a Stream of Helium

There are no significant differences between the spectrum of zeolite dehydrated at 515°C in helium and the spectrum of zeolite dehydrated at 350°C in vacuum. Thus, Co siting in zeolites prepared by dehydration at 350°C corresponded to Co siting in the zeolite at the start of the catalytic testing for the selective reduction of NO by methane that will be described in the next quarterly report (see also the catalytic testing described in Ref. 6).

### 2.3.2. Temperature Dependence of Dehydration of Co-ZSM-5 in Vacuum

The spectra of Co-ZSM-5/28 zeolite dehydrated in vacuum at temperatures ranging from 30°C to 540°C are present in Figures 22 and 23. The spectrum for the zeolite evacuated at room temperature corresponded to the spectrum of a hydrated sample with only a low intensity band at 19,500  $\text{cm}^{-1}$ . The spectrum of the sample dehydrated at 100°C exhibited features characteristic for hydrated zeolite and of the zeolite dehydrated at 350°C and represents the transition stage of dehydration of Co-ZSM-5 samples. Samples dehydrated at temperatures from 180 to 360°C were similar, and the spectra correspond to that of a sample dehydrated at standard conditions (vacuum for 3h at 350°C). Spectra of samples dehydrated at high temperatures (424-540°C) exhibited different fine structure than spectra obtained with a sample dehydrated at standard condition. Moreover, at temperatures higher than 500°C, a new band at 25,000  $\text{cm}^{-1}$  appeared in spectra of Co-ZSM-5 zeolites (cf. Section 2.2.1). In the case of Co-ZSM-5/28, this band was difficult to observe, probably due to low Co concentration in the zeolite.

It is evident that there are two different Co siting in Co-ZSM-5 depending on conditions of dehydration of sample. One siting is characteristic for dehydration at 350°C

in vacuum or for dehydration in a stream of helium at 500°C, while the second one can be created by dehydration in vacuum at temperatures higher than 450°C.

## 2.4. Co-Erionite

### 2.4.1. Co-Erionite Dehydrated at 350°C

The spectrum of Co-erionite dehydrated at 350°C, with bands centered at 15,500, 16,400 and 18,200  $\text{cm}^{-1}$ , is given in Figure 24a. The analysis of this spectrum *via* second derivative mode analysis (Figure 24b) indicates the possible presence of six bands at 15,900, 17,350, 18,850, 19,500, 20,500 and 21,200  $\text{cm}^{-1}$ . It is evident that the Co-erionite spectrum is simpler than the spectrum of Co-ZSM-5. The second derivative of Co-erionite (Figure 24b) appear to correspond to some of the bands present in the second derivative spectrum of Co-ZSM-5 dehydrated at 350°C (Figure 8). These similarities in the spectra can help to attribute the bands in the spectrum of Co-ZSM-5 to individual Co sites in the ZSM-5 matrix. Moreover, the simpler spectrum of Co-erionite provides the opportunity to identify the Co(II) sites that give rise to this Co(II) spectrum. Thus, investigation of Co-erionite might be the key point to determination of Co(II) sites in ZSM-5.

The verification of the presence of six bands (observed only by second derivative analysis) in the spectrum requires further experiments, mainly determination of the concentration dependence of spectra of Co-erionite. The presence of identical bands in the spectrum of Co-erionite and -ZSM-5 (indicating similarities in siting of some ions) verify the observation of identical bands in luminescence spectra of Cu(I)-ZSM-5 and -erionite [7,8].

### 2.4.2. Co-Erionite Dehydrated at 525°C

The spectrum of Co-erionite dehydrated at 525°C shown in Figure 24a, differs from the spectrum of erionite dehydrated at 350°C (Figures 25). A new band, split into a doublet



with maxima at 24,500 and 25,500  $\text{cm}^{-1}$  (Figure 26 and 27) appeared upon high temperature dehydration. In addition a shoulder indicating a band at 14,500  $\text{cm}^{-1}$  was now present in the complex band centered at 17,500  $\text{cm}^{-1}$ . This complex band exhibited similarities with the spectrum of Co-erionite dehydrated at 350°C and probably corresponds to Co ions located in the same environment as in the erionite dehydrated at 350°C.

The doublet centered at 25,000  $\text{cm}^{-1}$  indicates a new environment of Co(II) ions in Co-erionite dehydrated at 525°C. This band (as well as the band at 14,500  $\text{cm}^{-1}$ ) is characteristic of  $D_{3h}$  symmetry of Co(II) ions located in the plane of oxygens of regular six-ring windows of Co-A zeolite (cf. Ref 4). There are regular single six-rings in the erionite framework, but attribution of the Co-erionite spectral bands at 25,000  $\text{cm}^{-1}$  to Co(II) ions in this environment requires further confirmation (*via* adsorption of CO, water, and ethylene on these Co(II) ions).

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Figure 1

UV-VIS DR spectrum of Co-ZSM-5 with different Co content dehydrated at 350 °C

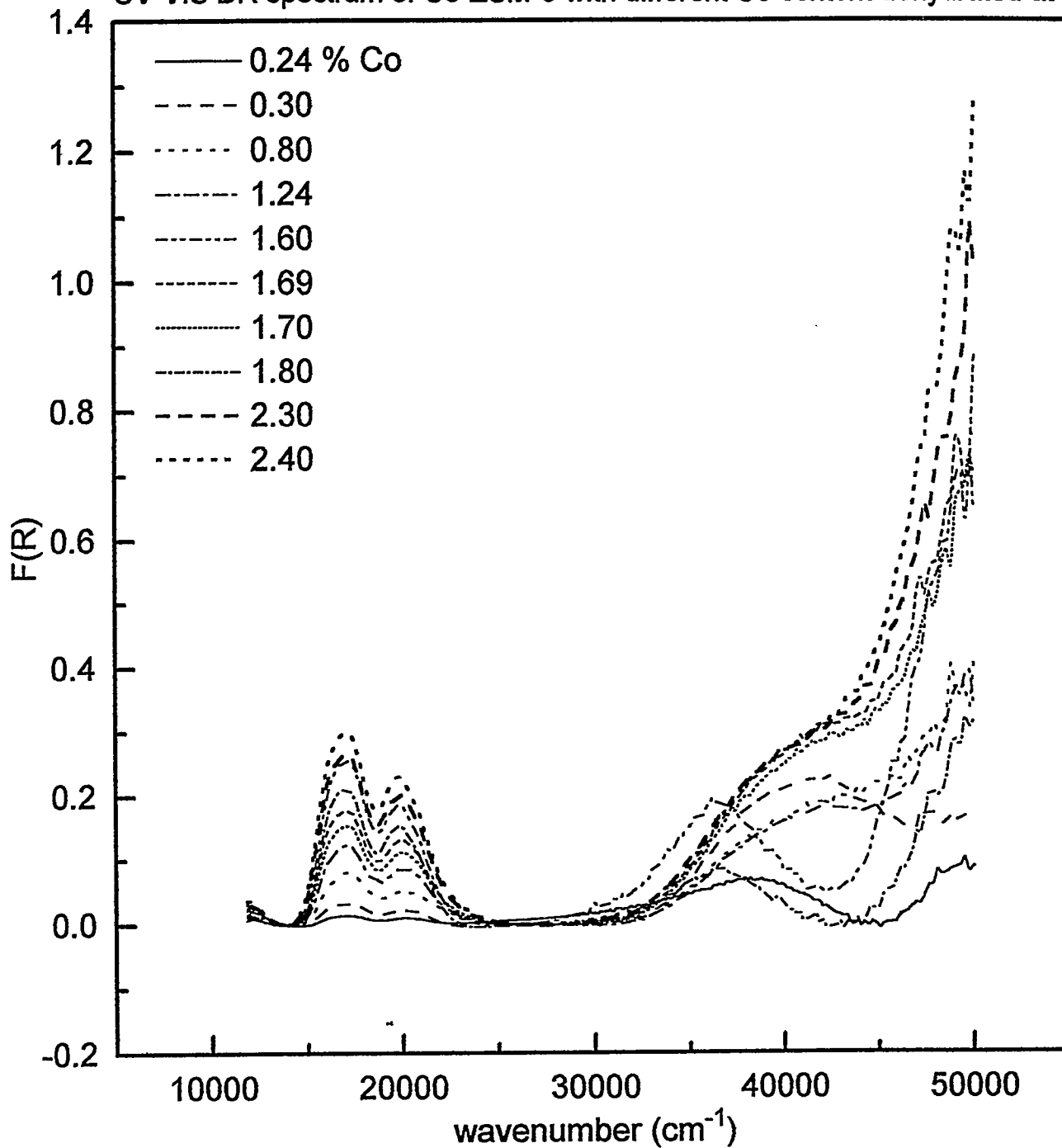


Figure 2  
VIS DR spectrum of Co-ZSM-5 dehydrated at 350 °C with different Co content,  
spectrum of parent zeolite was subtracted.

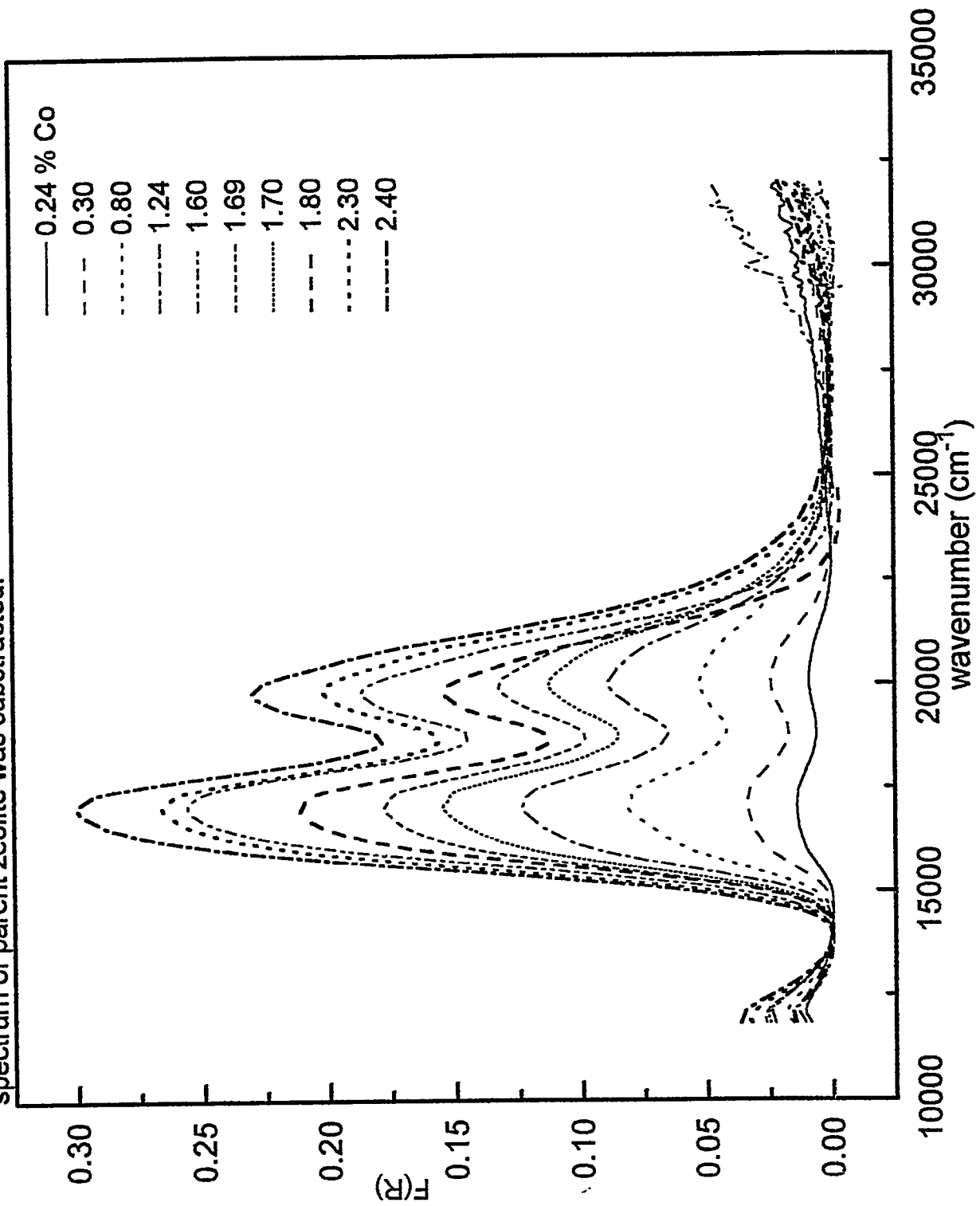


Figure 3

Normalized DR spectrum of Co-ZSM-5 with different Co content dehydrated at 350 °C in VIS region, spectrum of parent zeolite was subtracted, spectra were separately normalized to maximum intensity equal to 1.

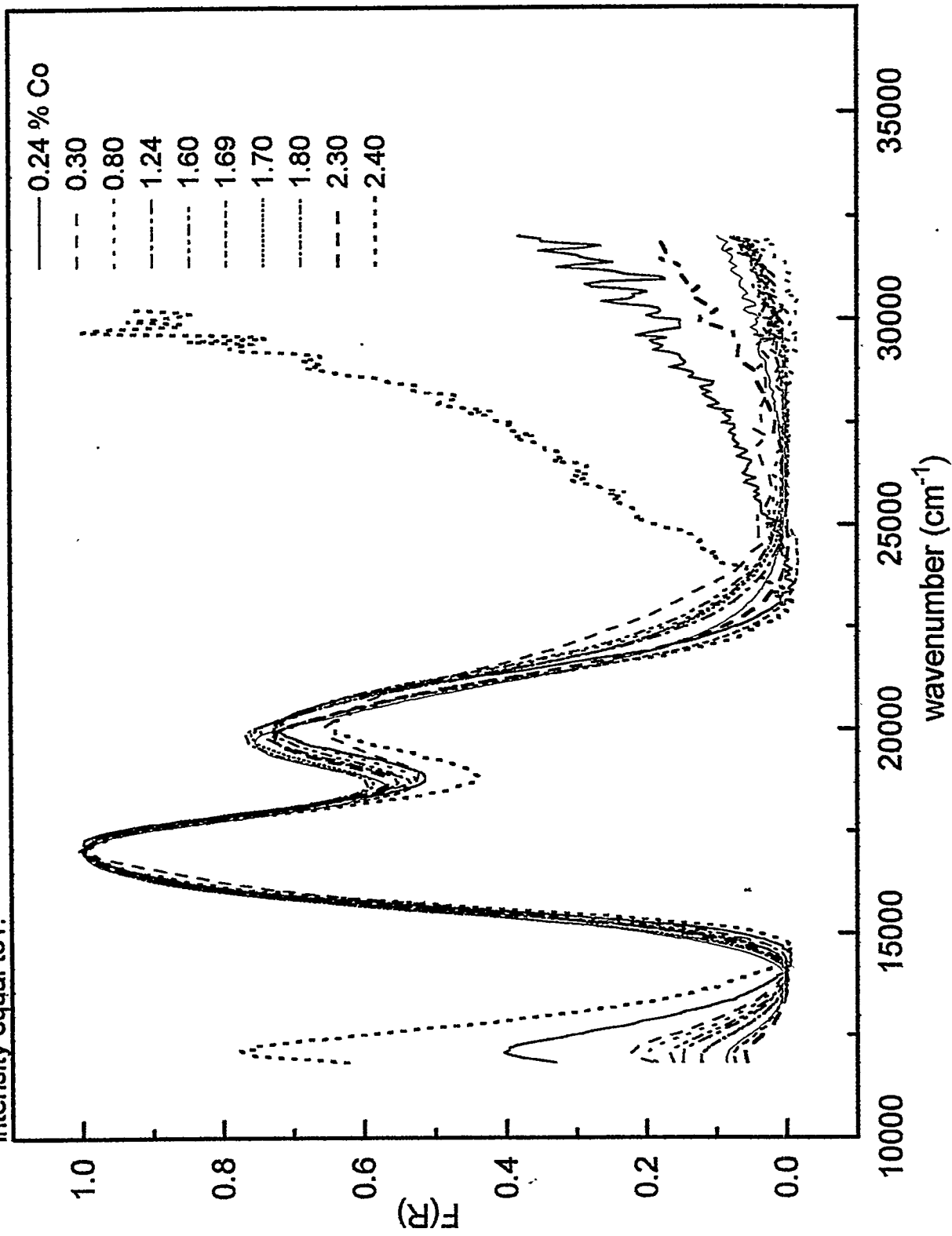


Figure 4  
Dependence of area of VIS absorption band of Co-ZSM-5 dehydrated at 350 °C  
on Co concentration

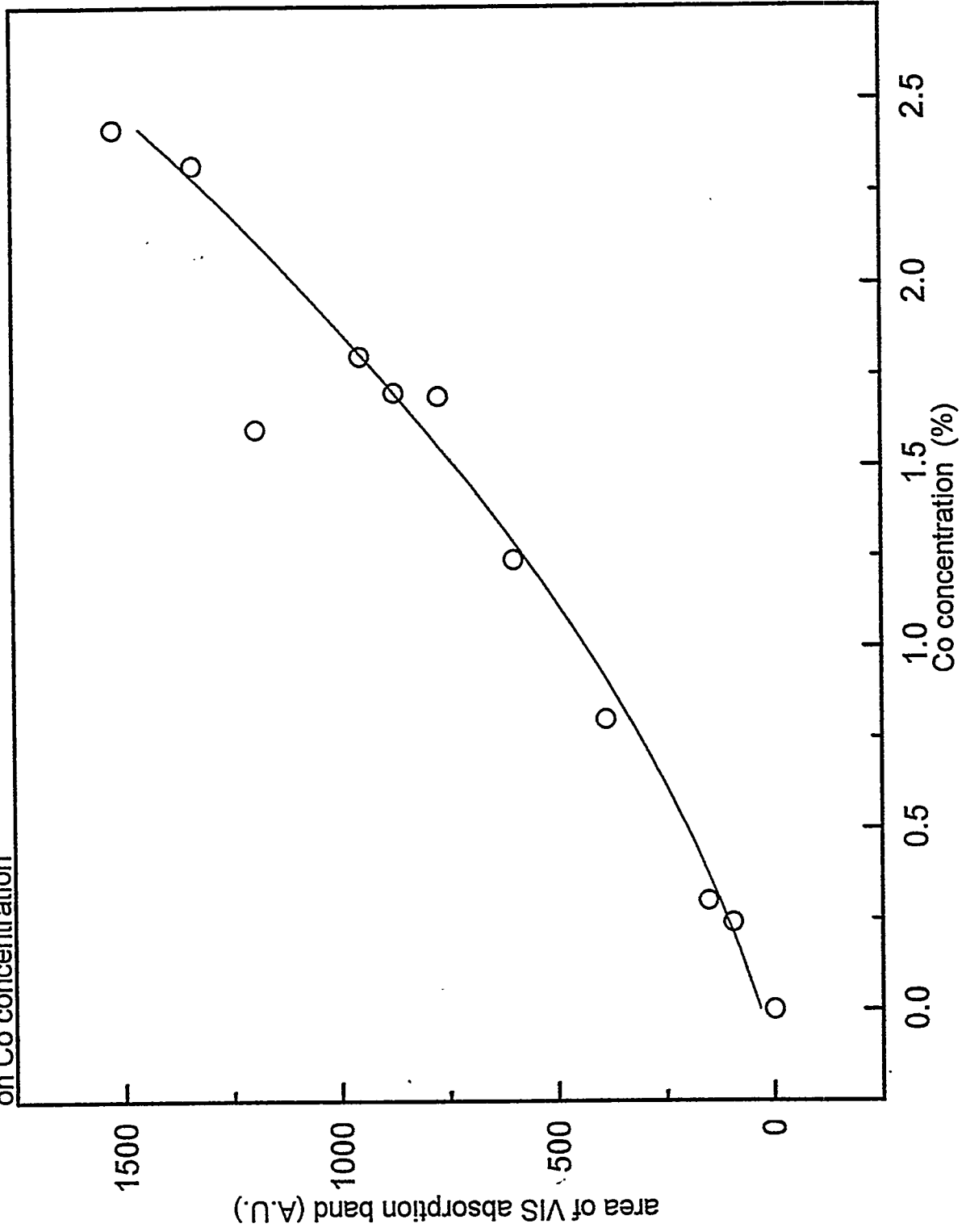


Figure 5  
Dependence of wavenumber of maximum B of Co-ZSM-5 dehydrated at 350 °C  
on Co concentration

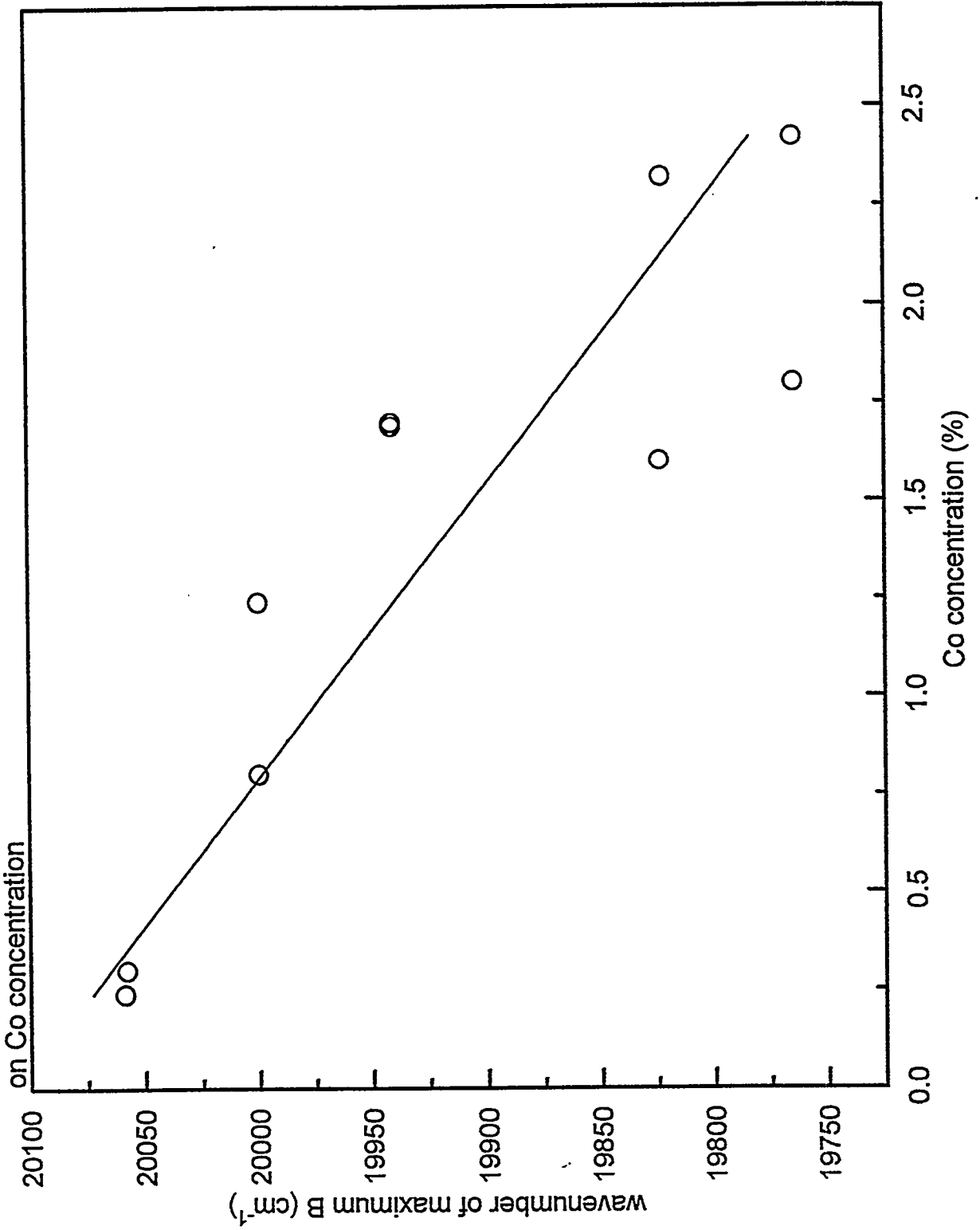


Figure 6  
Dependence of ratio of intensities in maximum B and A of Co-ZSM-5 dehydrated at 350 °C  
on Co concentration

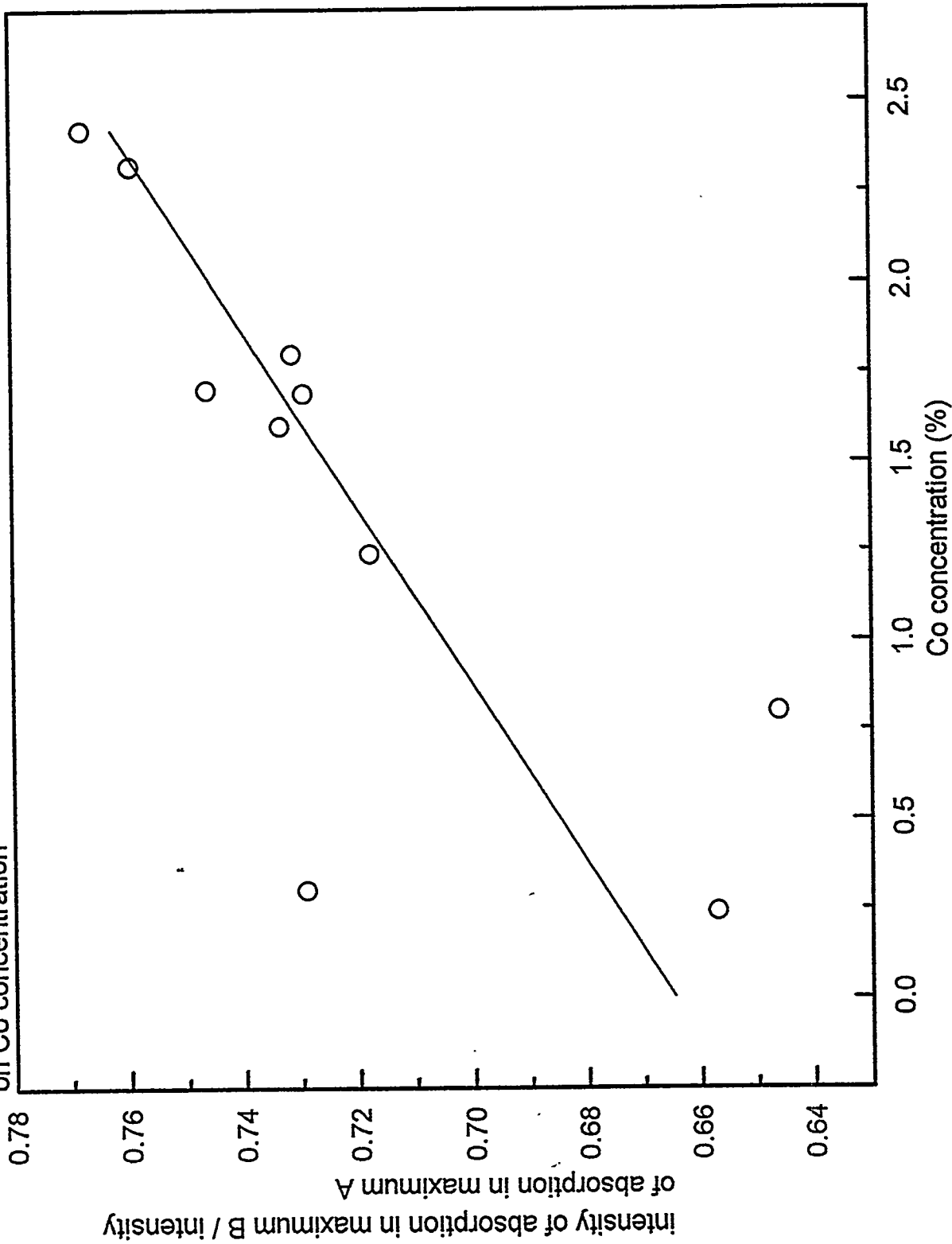


Figure 7  
VIS DR spectrum of fully hydrated Co-ZSM-5/35

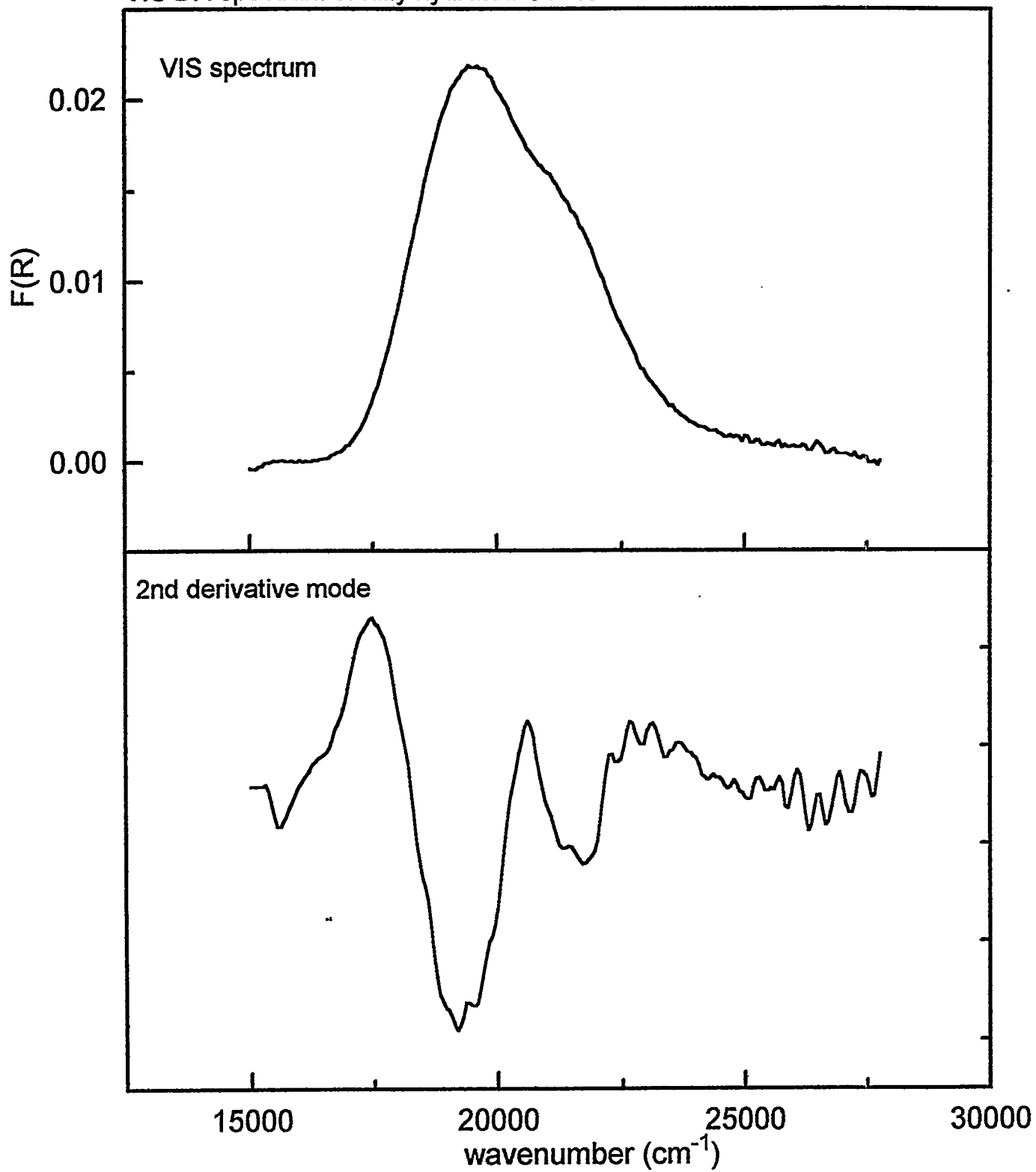




Figure 8  
2nd derivative mode of VIS DR spectra of Co-ZSM-5 with  
different Co content dehydrated at 350 °C

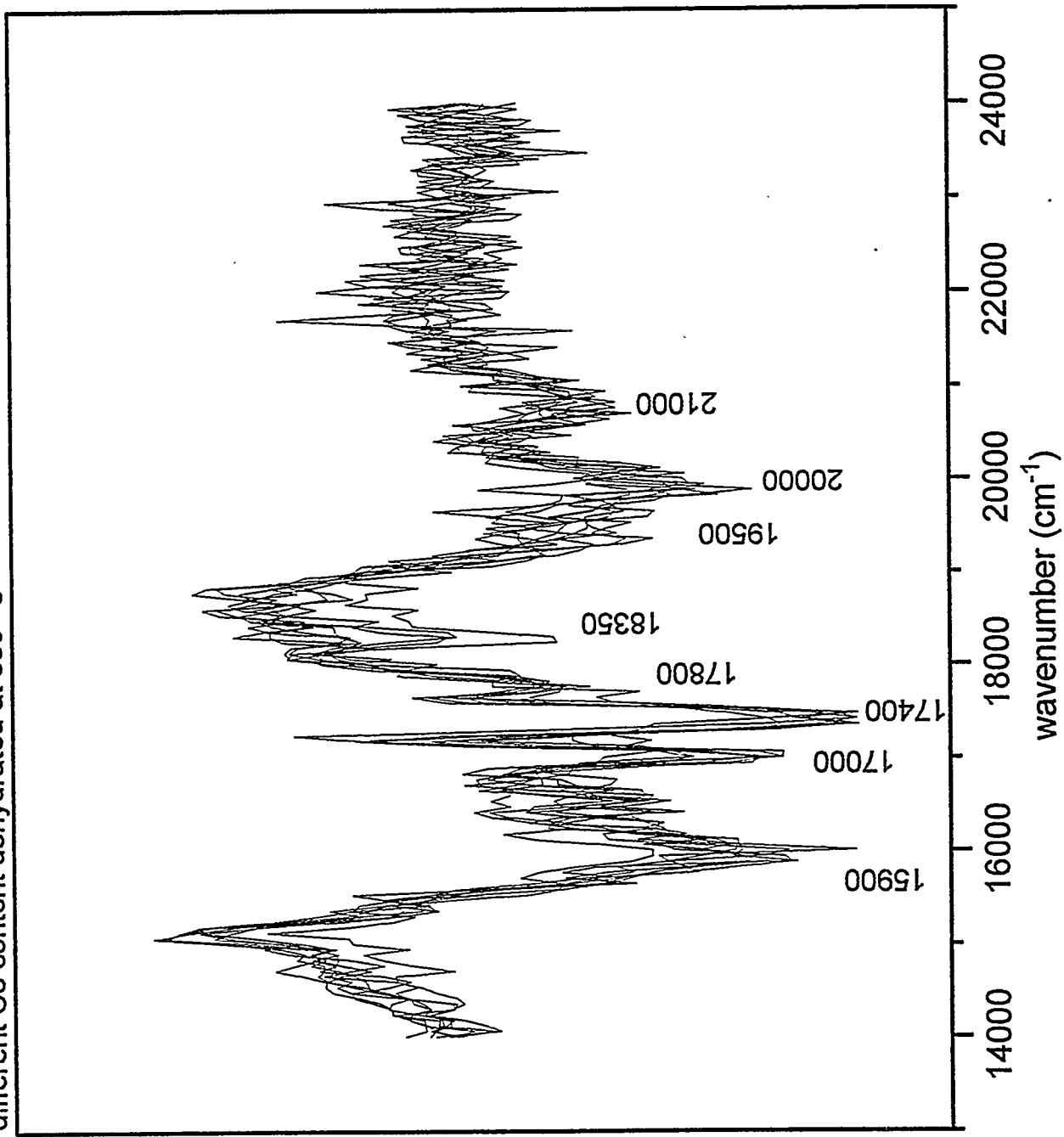


Figure 9  
VIS DR spectrum of Co-ZSM-5/43 dehydrated at 350 °C recorded at 85 K

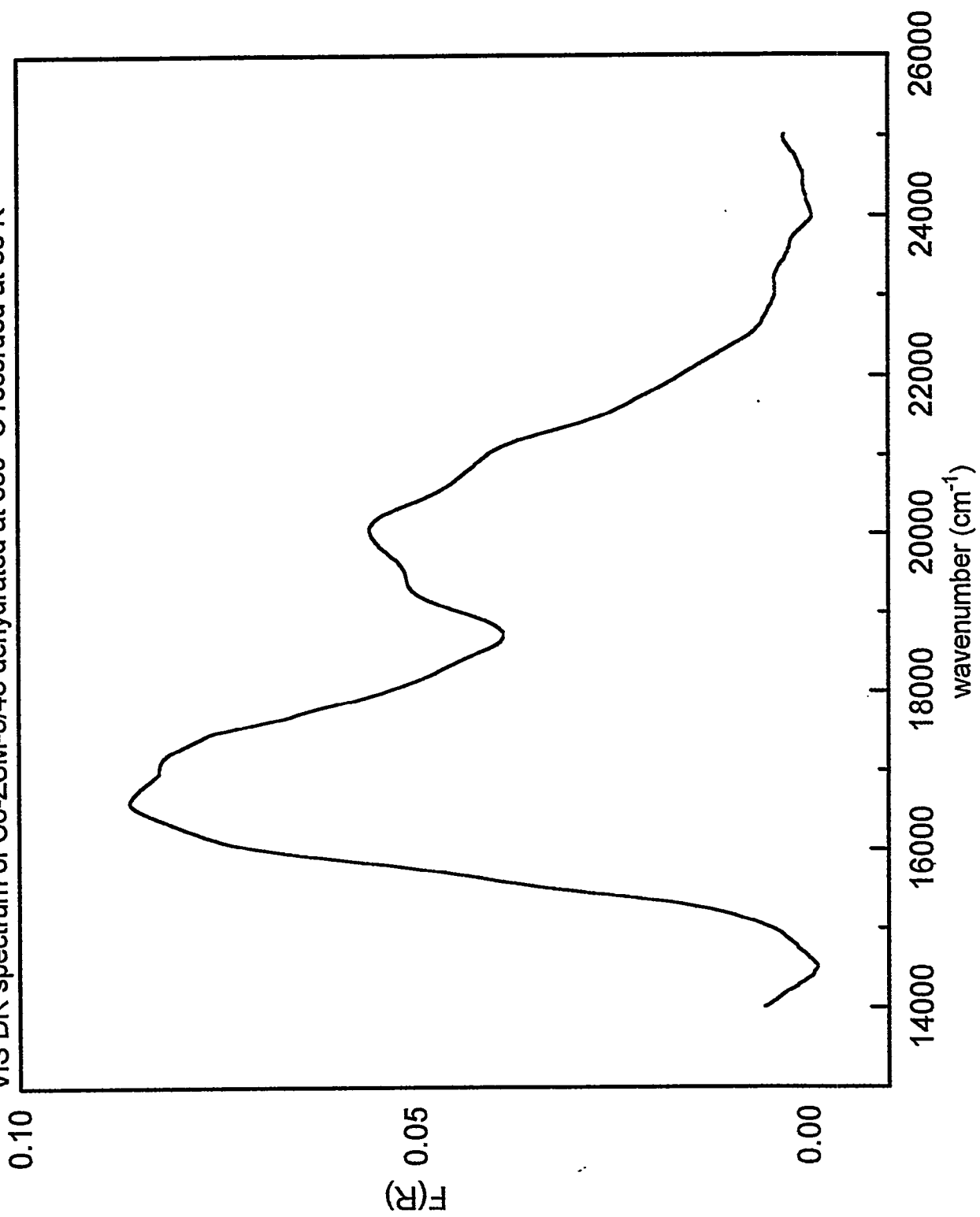


Figure 10  
2nd derivative mode of VIS DR spectrum of Co-ZSM-5/43  
dehydrated at 350 °C, recorded at 80 K

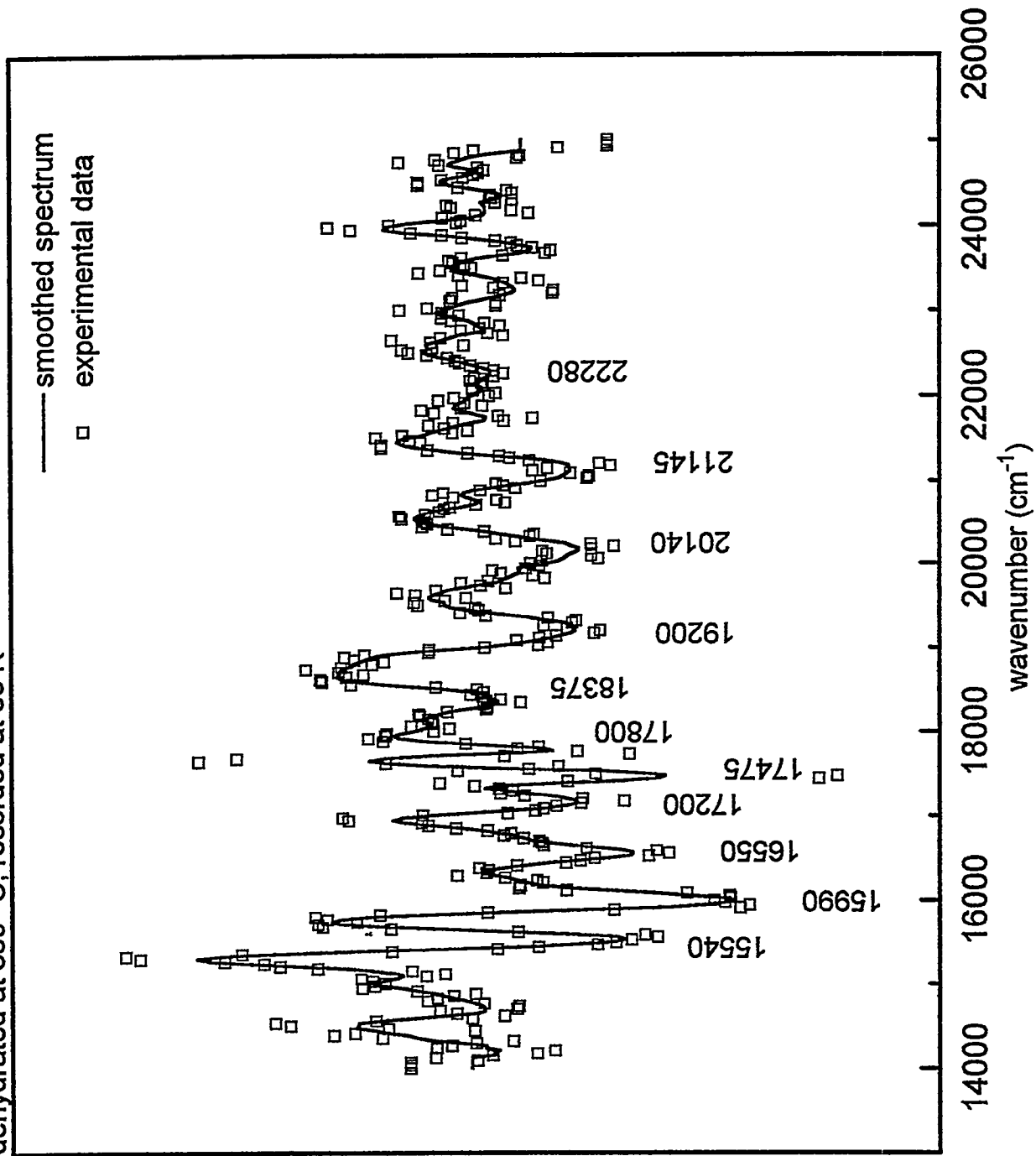


Figure 11  
Effect of CO adsorption on UV-VIS DR spectra of Co-ZSM-5/45 dehydrated at 350 °C

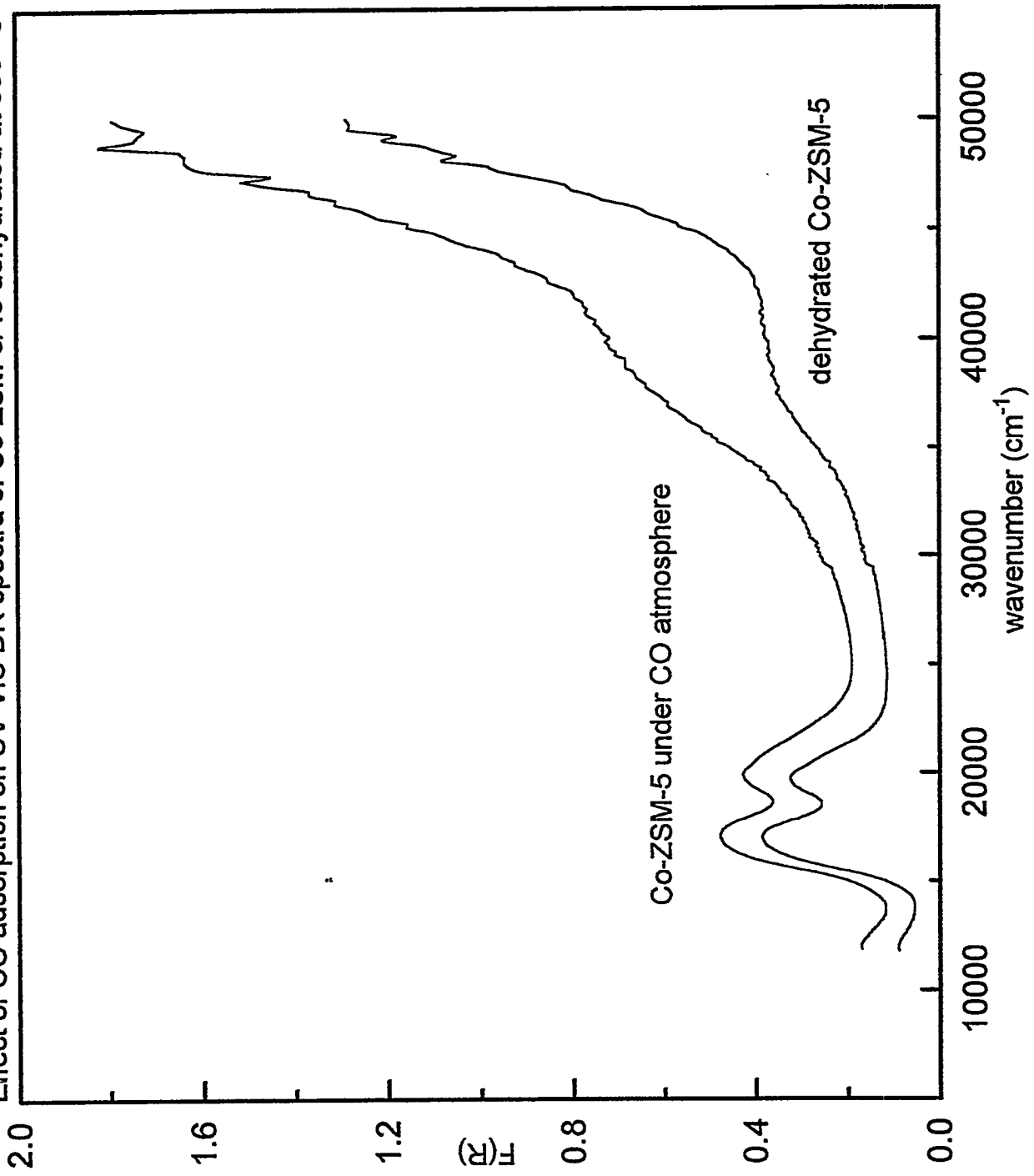


Figure 12

Effect of water adsorption on UV-VIS DR spectra of Co-ZSM-5/45 dehydrated at 350 °C.

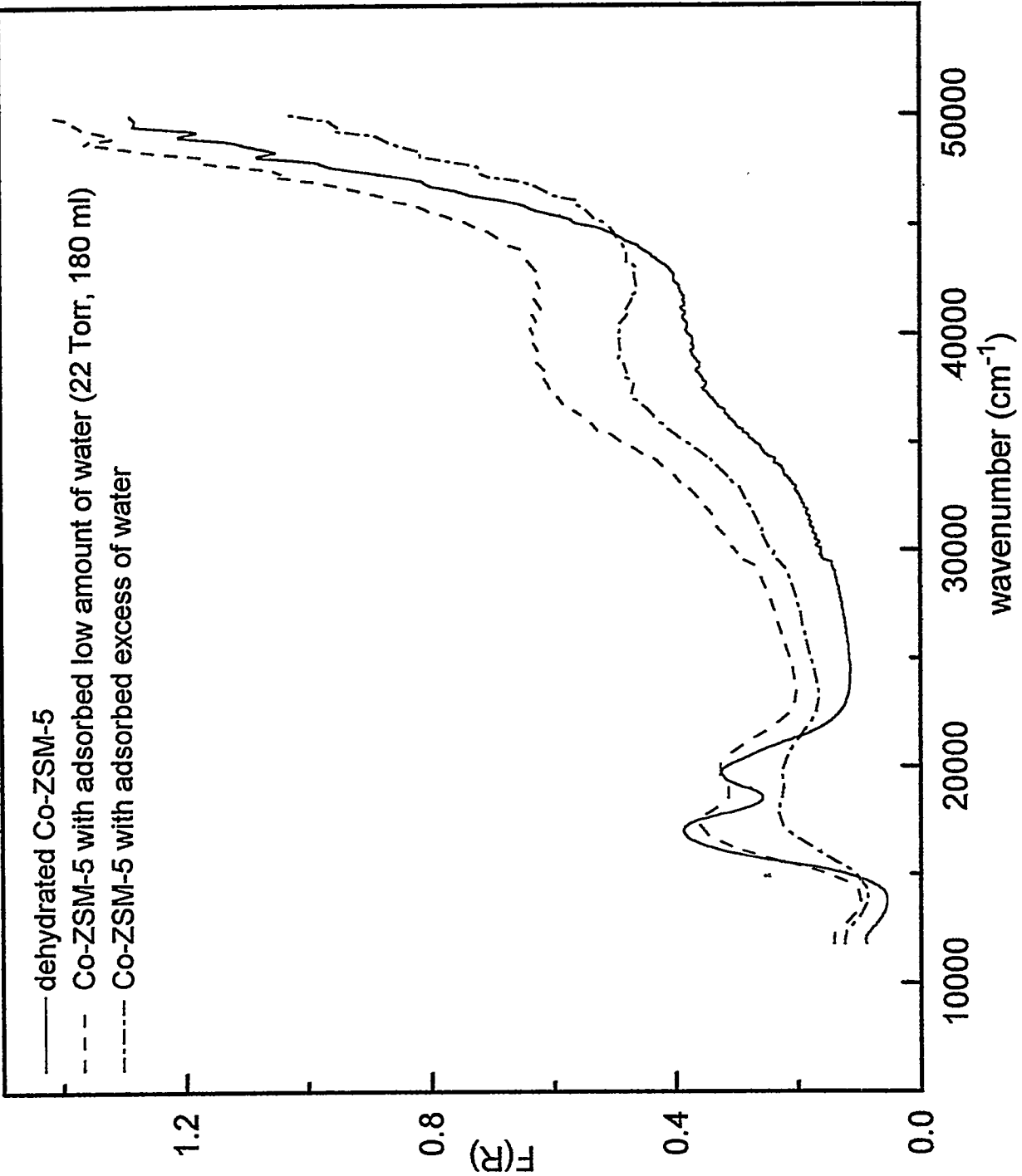


Figure 13

Effect of water adsorption on VIS DR spectra of Co-ZSM-5/45 dehydrated at 350 °C, spectrum of parent zeolite dehydrated at the same conditions was subtracted.

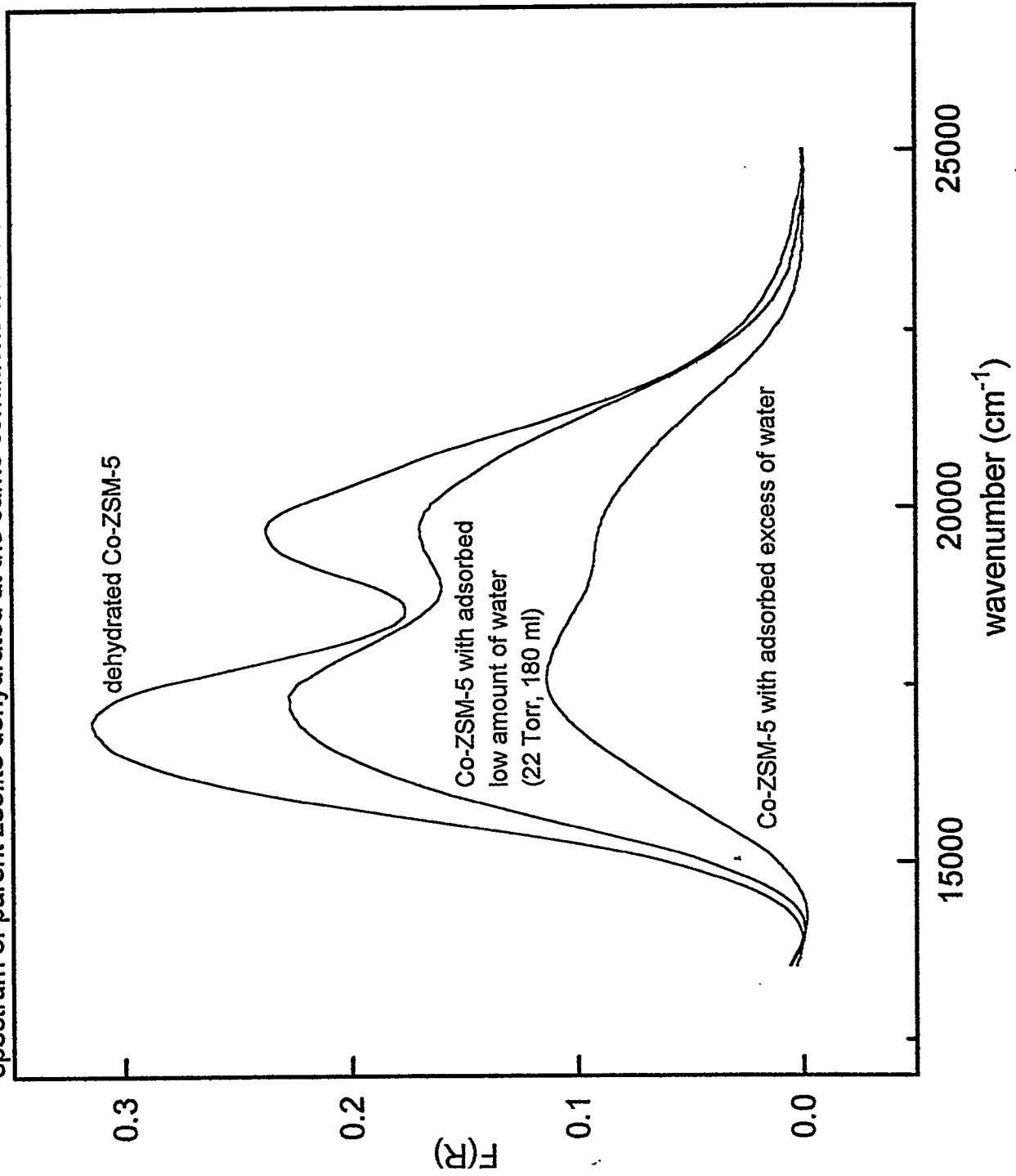


Figure14  
UV-VIS DR spectrum of Co-ZSM-5/30 dehydrated at 525 °C.

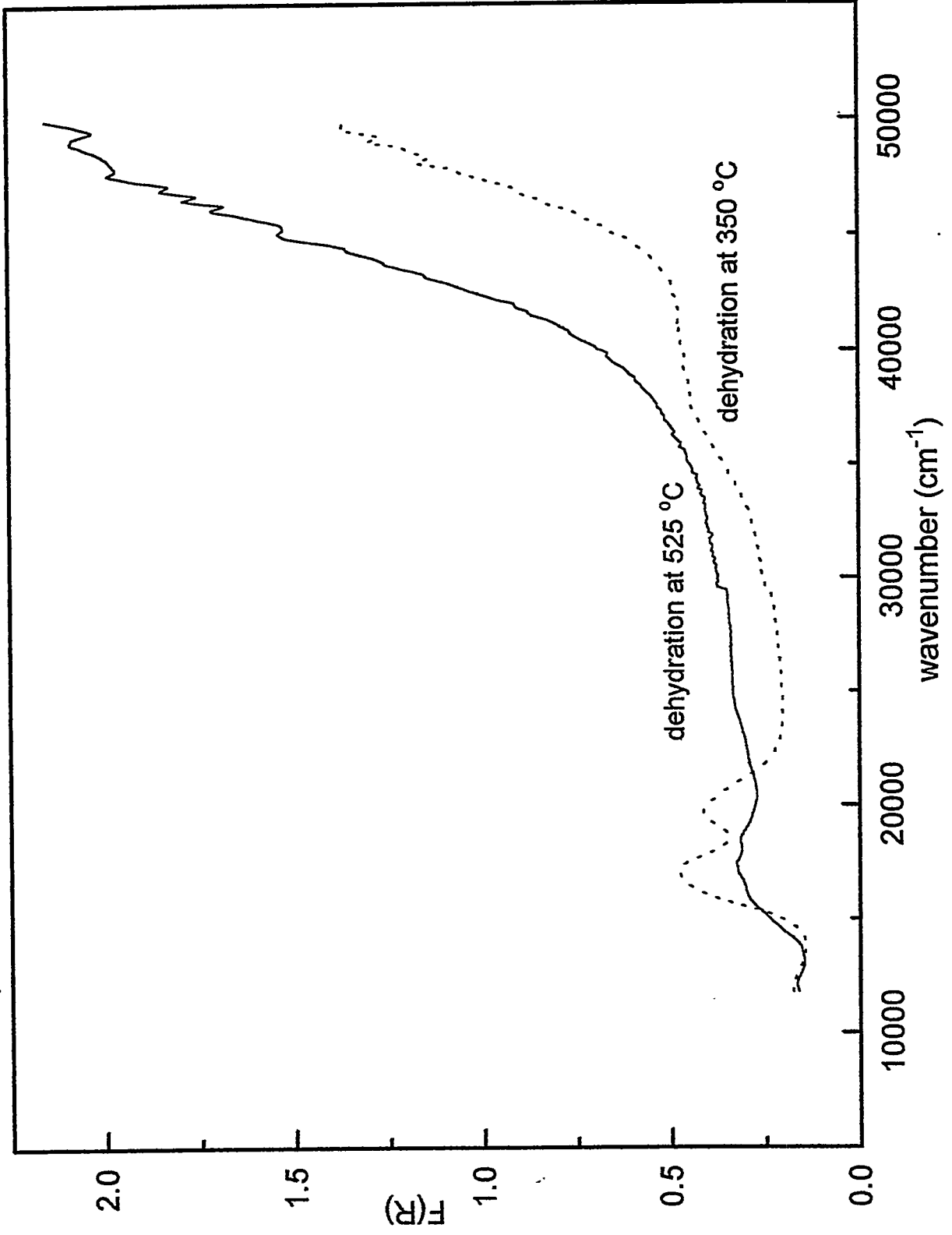


Figure 15

VIS DR spectrum of Co-ZSM-5/30 dehydrated at 525 °C, spectrum of parent zeolite was subtracted.

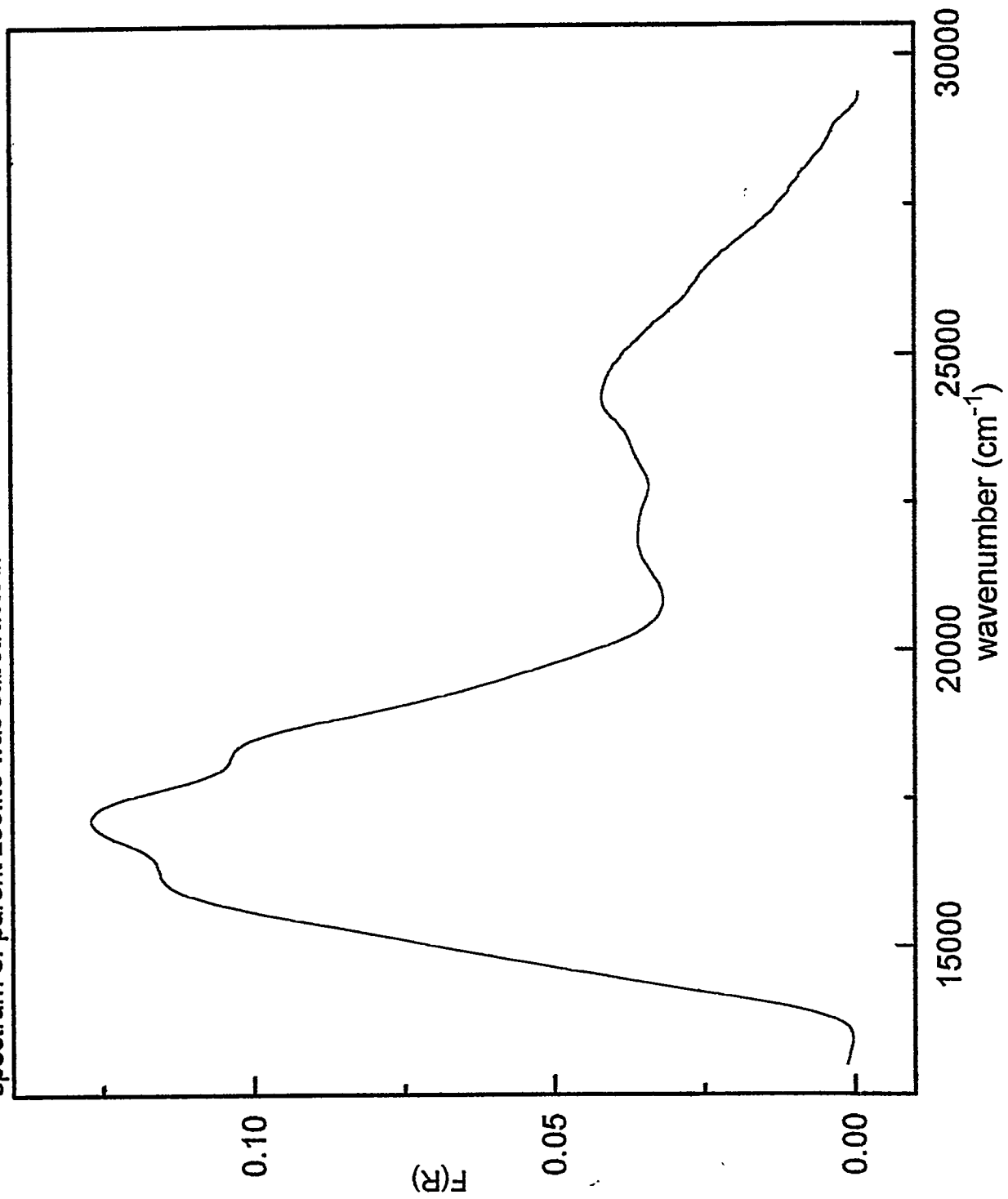




Figure 16

Effect of CO adsorption on UV-VIS DR spectrum of Co-ZSM-5/30 dehydrated at 525 °C.

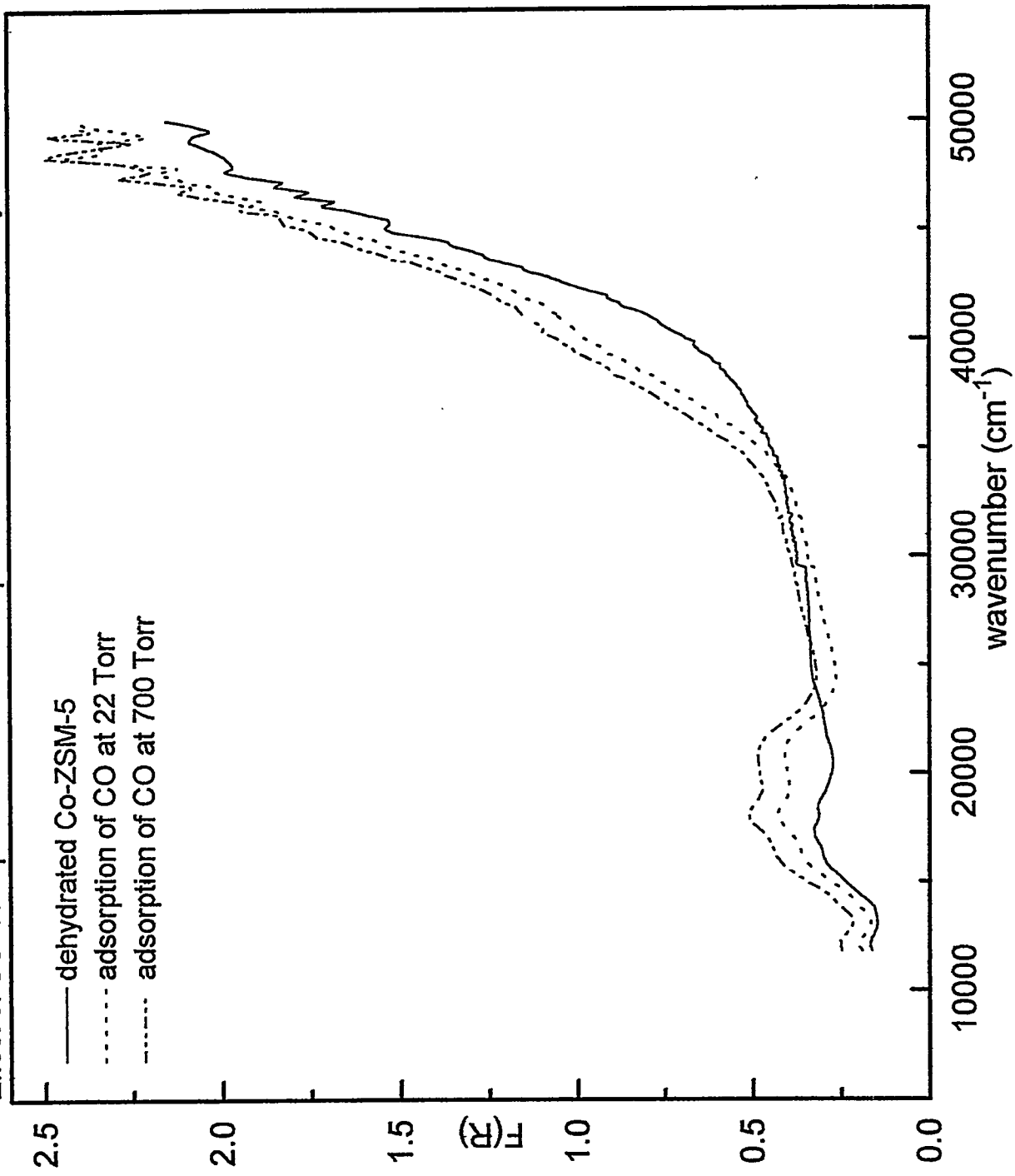


Figure 17  
Effect of CO adsorption on VIS DR spectrum of Co-ZSM-5/30 dehydrated at 525 °C,  
spectrum of parent zeolite was subtracted.

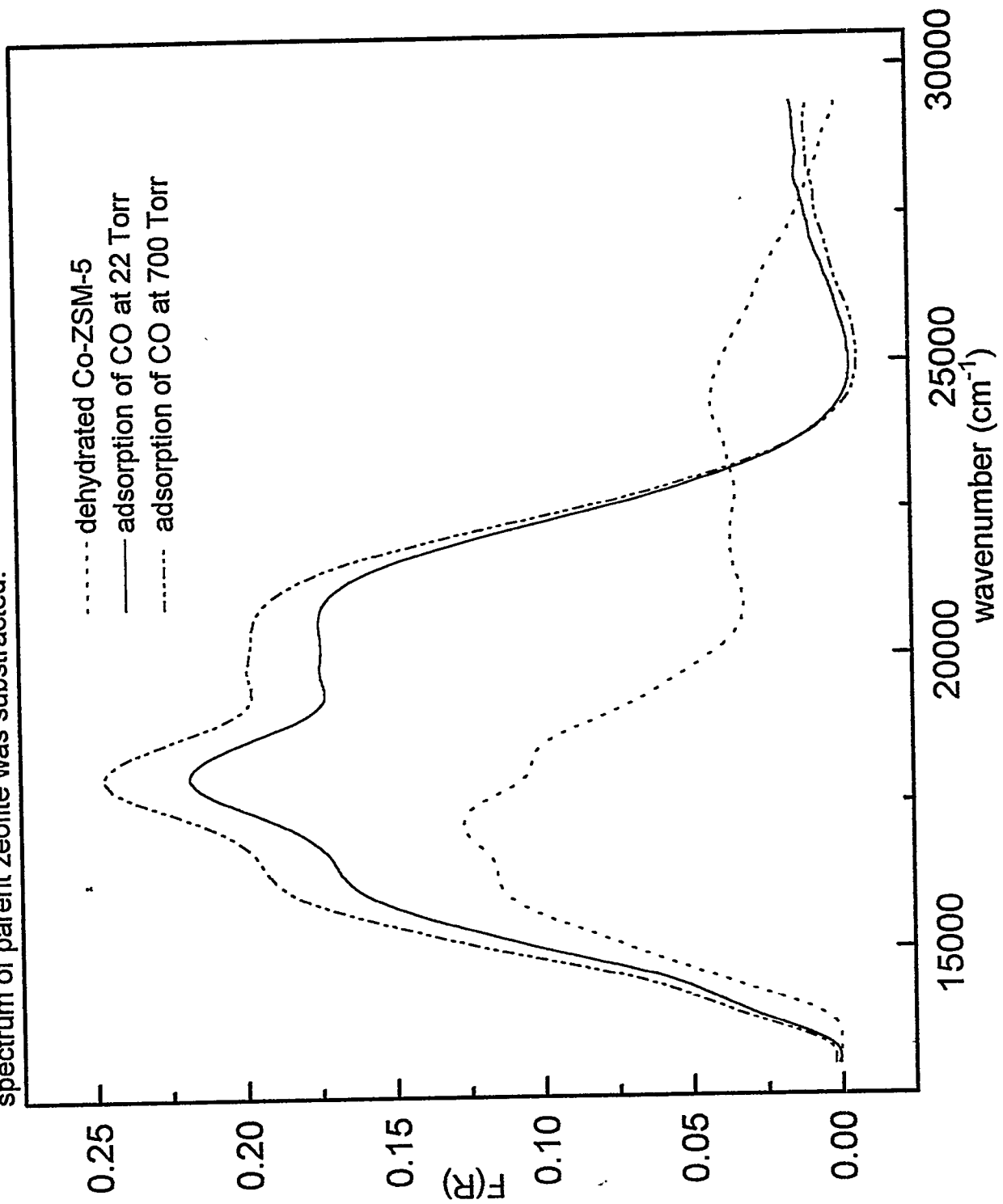


Figure 18

Effect of water adsorption on UV-VIS DR spectrum of Co-ZSM-5/30 dehydrated at 525 °C.

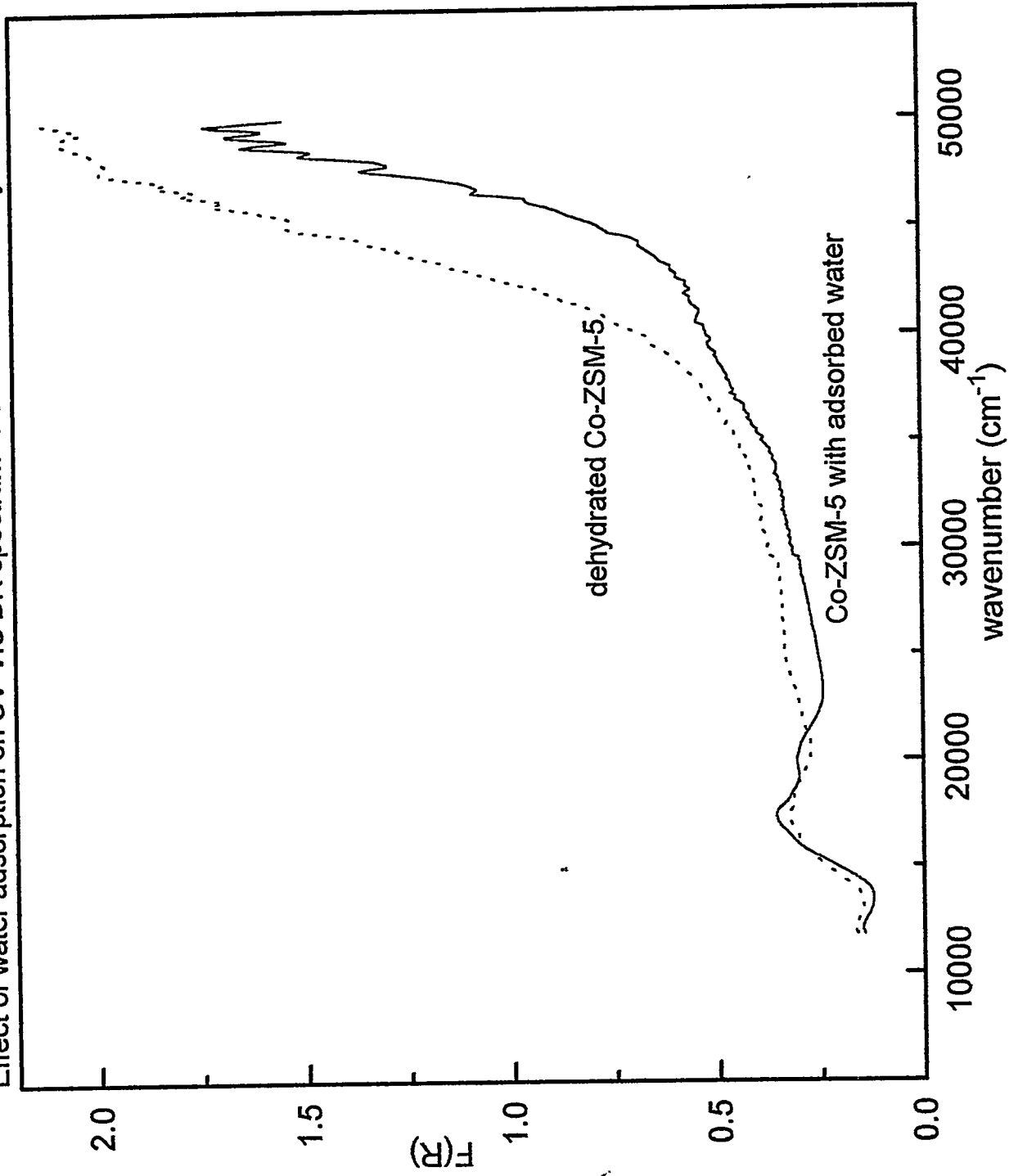


Figure 19

Effect of water adsorption on DR spectrum of Co-ZSM-5/30 dehydrated at 525 °C, spectrum of parent zeolite prepared at the same conditions was subtracted.

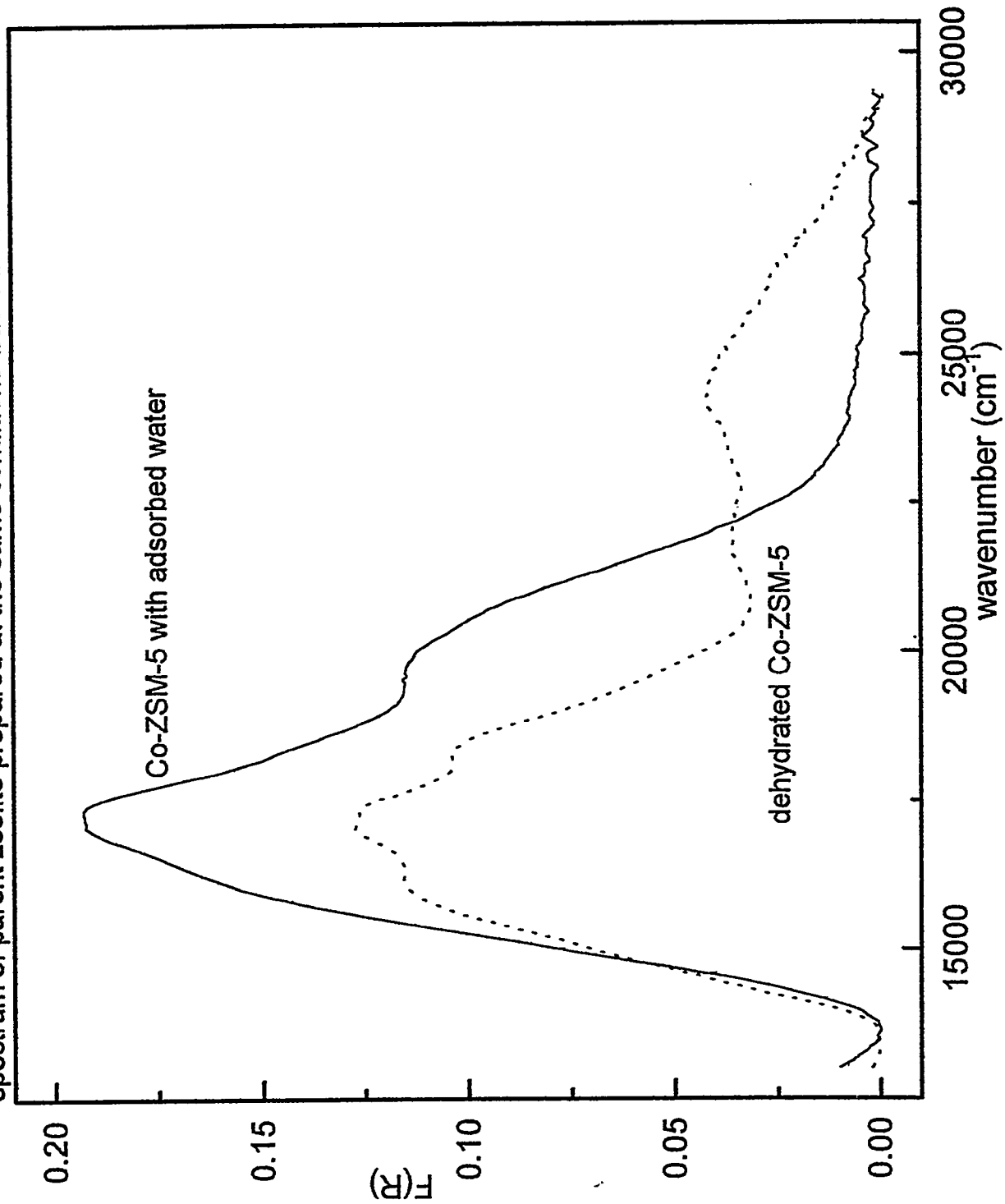


Figure 20

Effect of ethylene adsorption on UV-VIS DR spectrum of Co-ZSM-5/30 dehydrated at 525 °C.

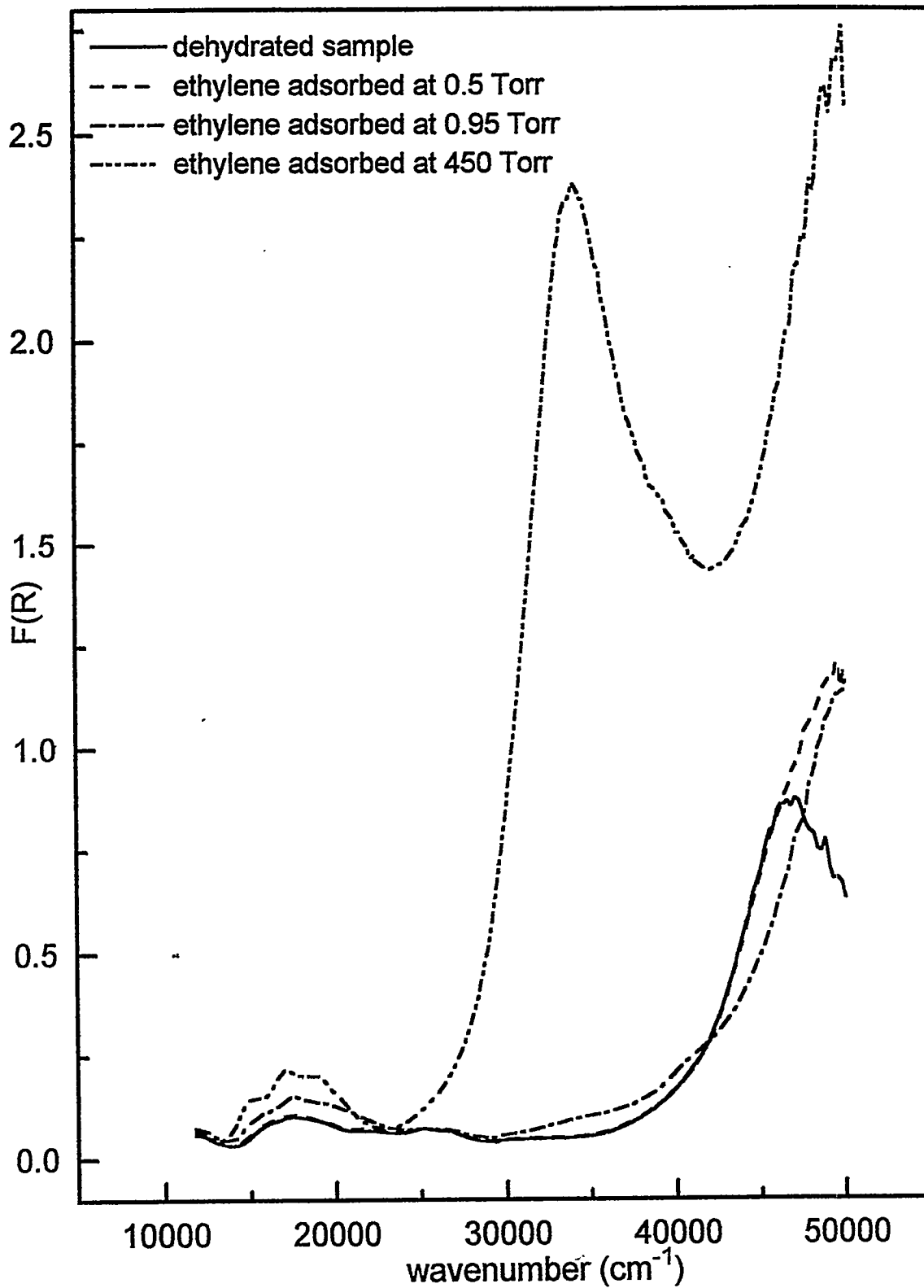


Figure 21  
Effect of ethylene adsorption on VIS DR spectrum of Co-ZSM-5/30 dehydrated at 525 °C,  
spectrum of parent zeolite was subtracted.

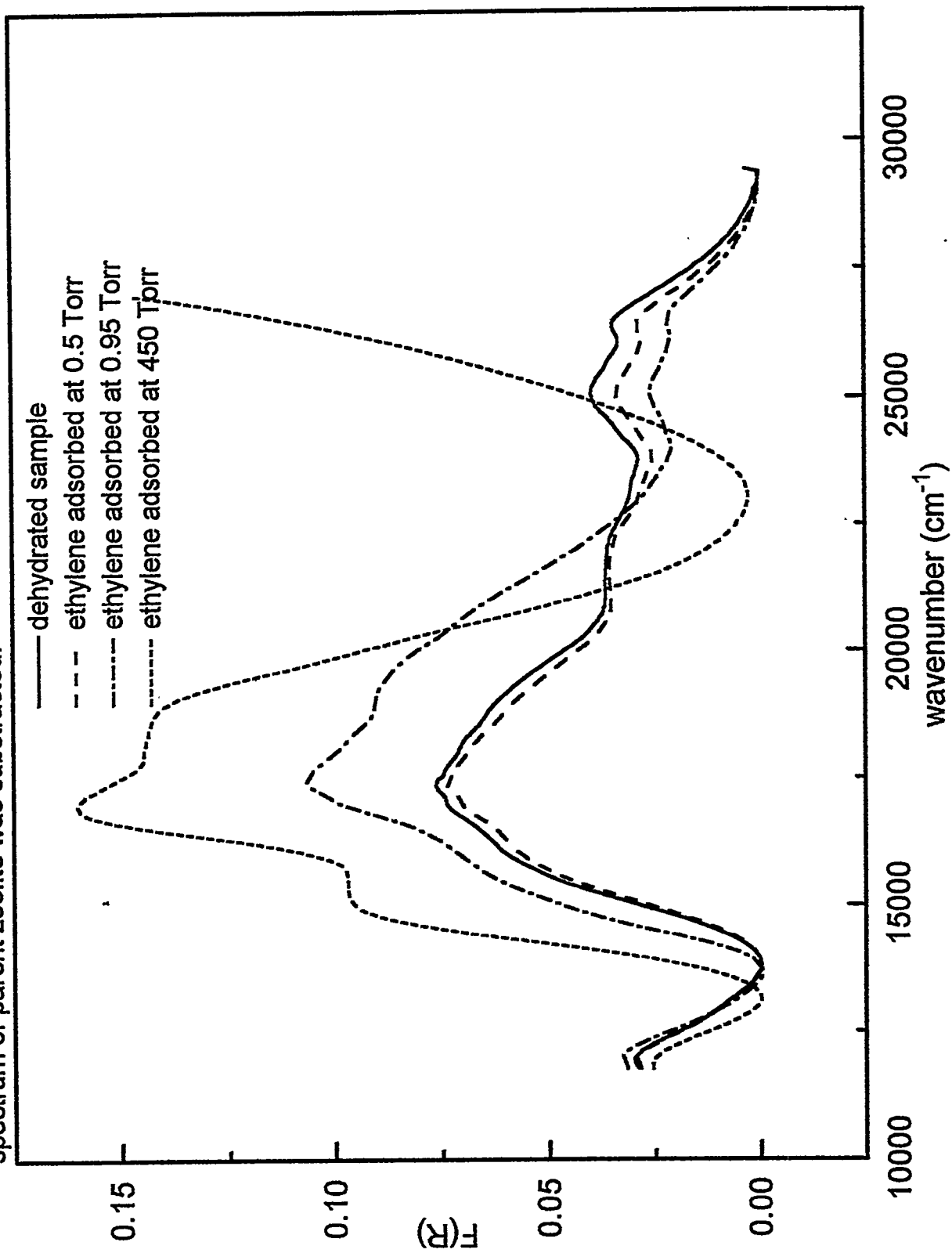


Figure 22

Dependence of UV-VIS DR spectrum of Co-ZSM-5/28  
on dehydration temperature

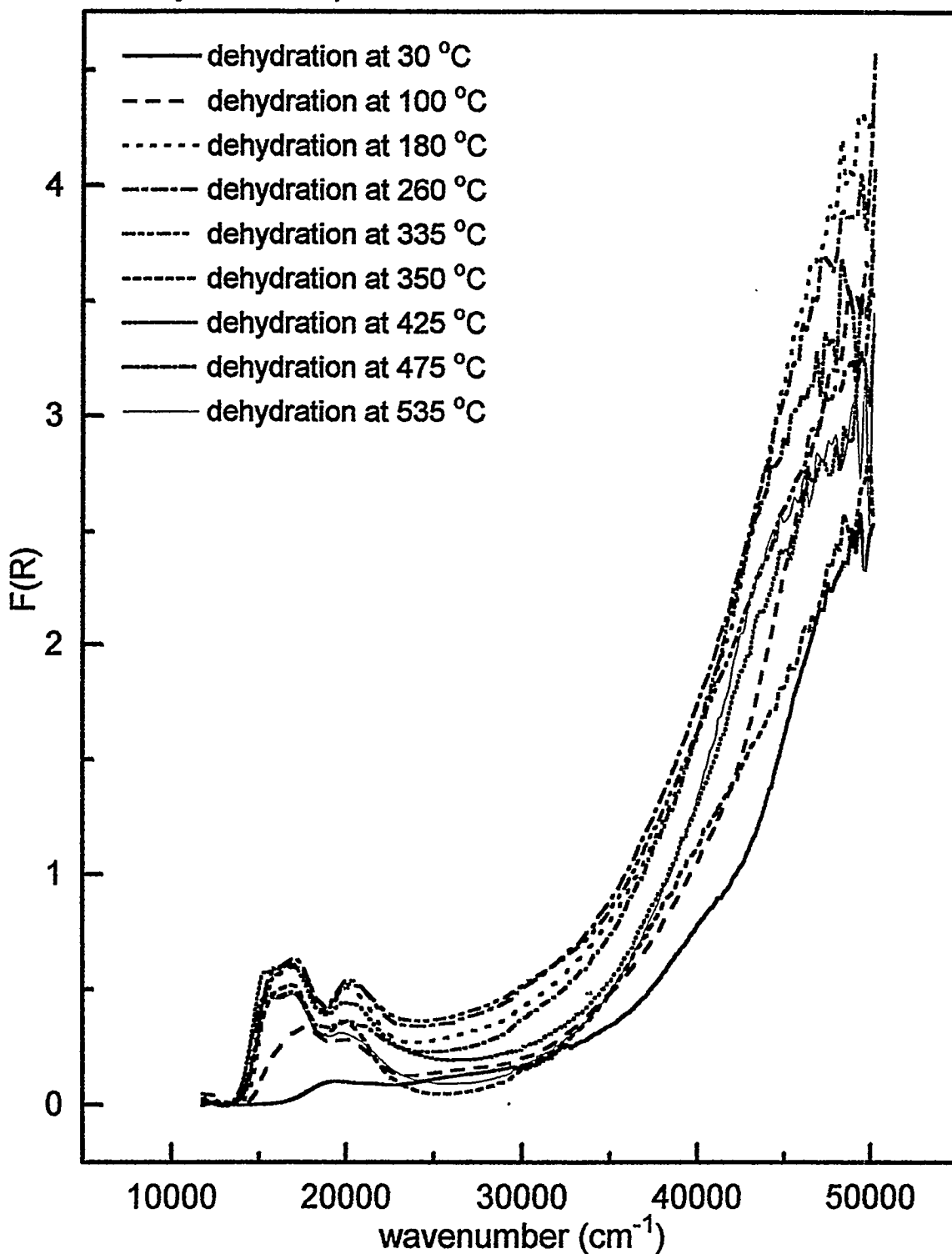


Figure 23

Dependence of VIS DR spectrum of Co-ZSM-5/28 on dehydration temperature, spectrum of parent zeolite dehydrated at similar conditions was subtracted.

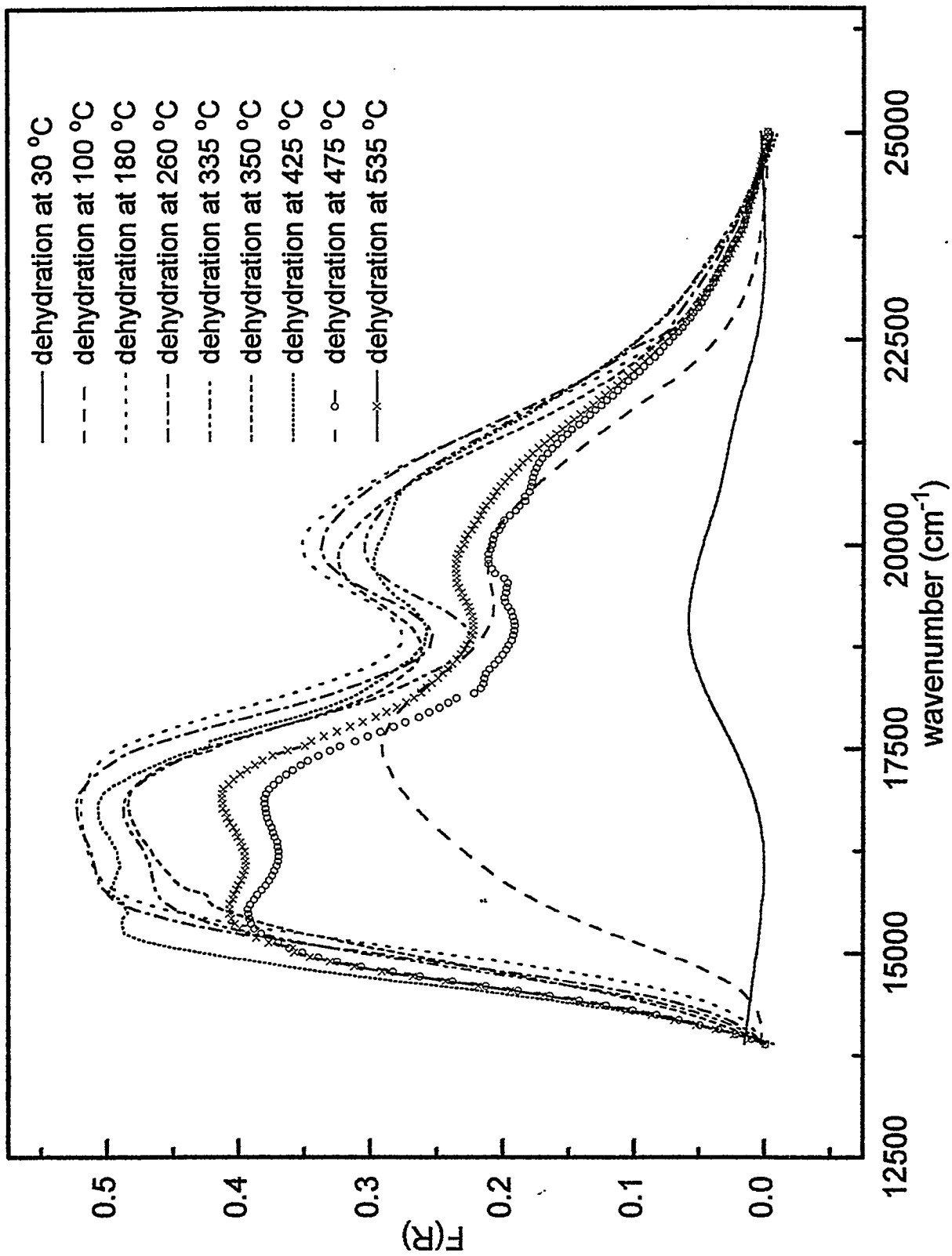




Fig 24

VIS DR spectrum of Co-erionite dehydrated at 350 °C,  
spectrum of parent zeolite was subtracted.

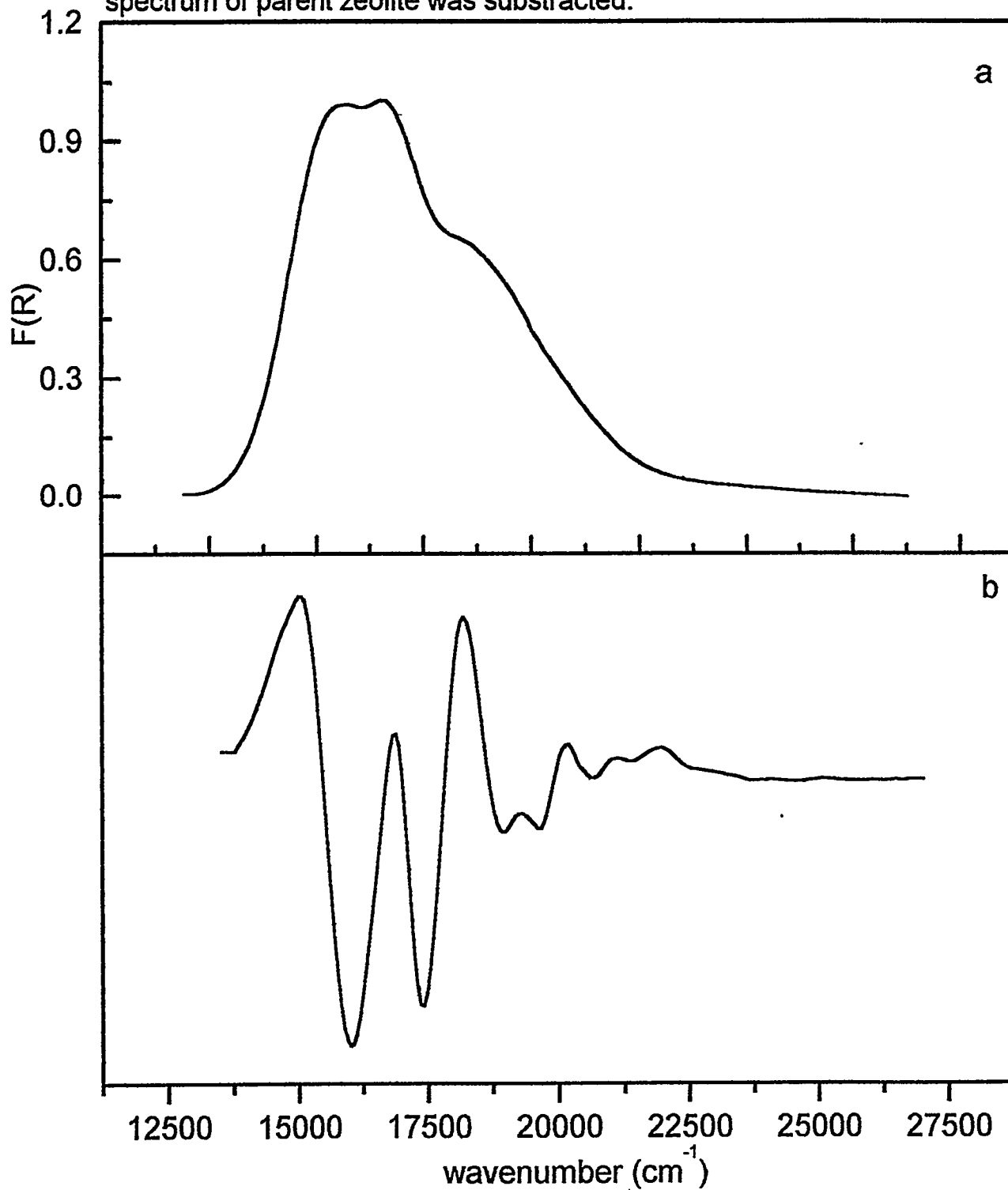


Figure 25  
UV-VIS DR spectrum of Co-erionite dehydrated at 525 °C

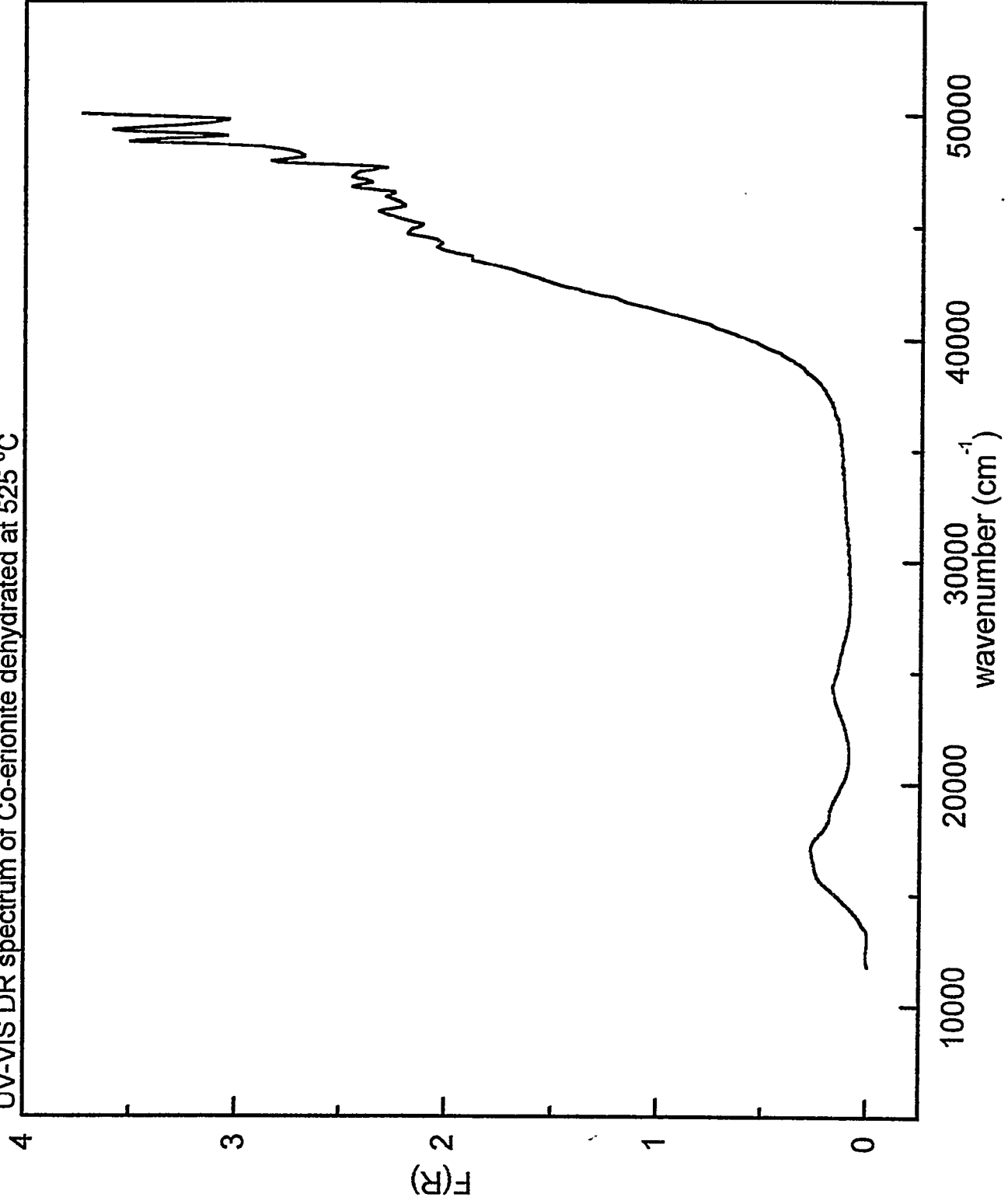


Figure 26

VIS DR spectrum of Co-erionite dehydrated at 525 °C.  
spectrum of parent zeolite was subtracted.

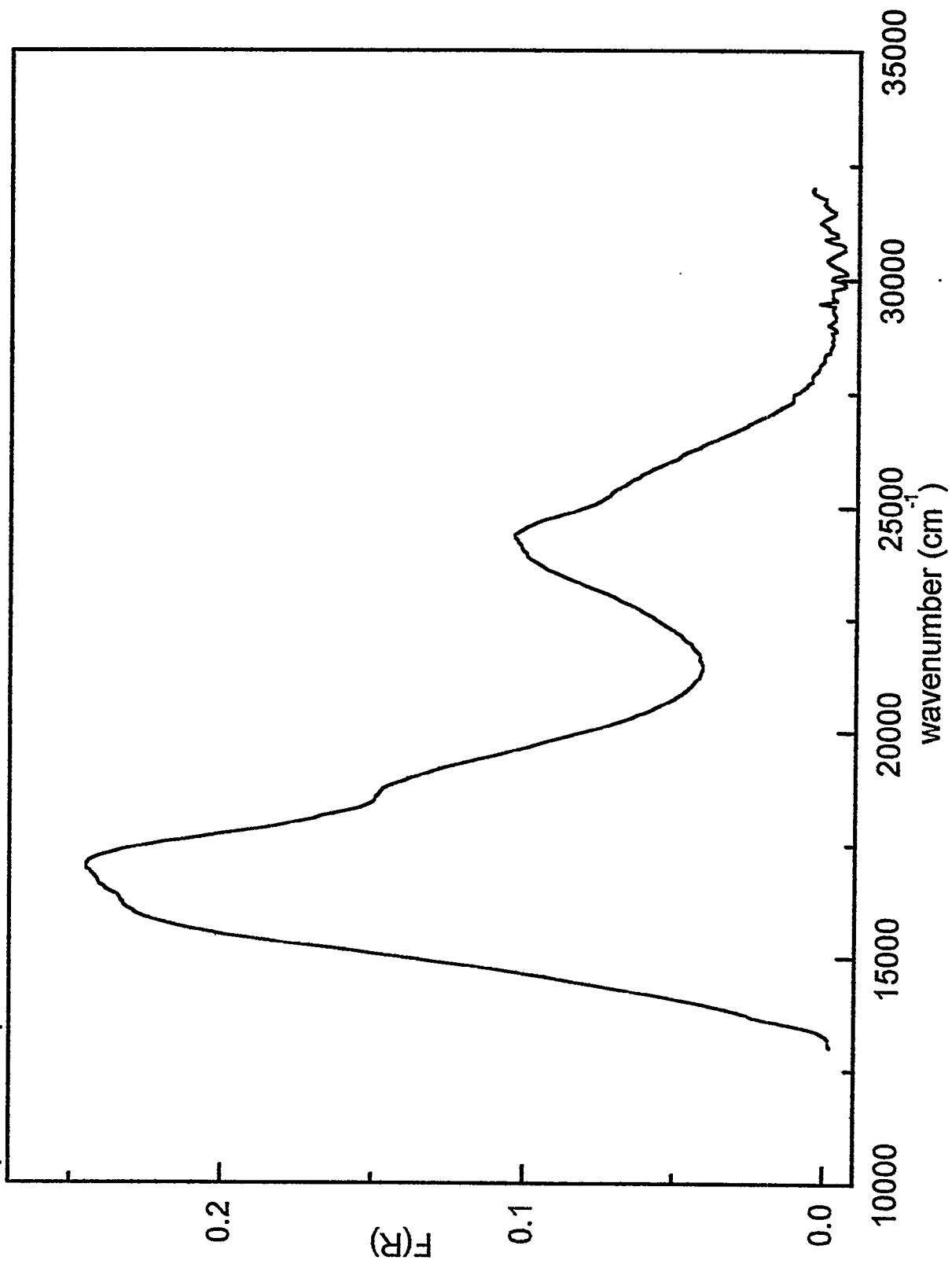


Figure 27

2nd derivative mode of VIS DR spectrum of Co-erionite dehydrated at 525 °C

