

**NO DECOMPOSITION IN NON-REDUCING ATMOSPHERES**

Technical Progress Report for the Period  
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### SUMMARY OF TECHNICAL PROGRESS

In the last quarterly technical progress report, it was shown that adsorption of CO and ethylene onto 0.2 wt% Co(II) ion exchanged erionite, with Si/Al molar ratio of 3.6, after dehydration at 350°C significantly altered the optical spectrum of the zeolite. It was also found that the paramagnetic moment of Co(II) in erionite (8 wt% Co(II)) dehydrated at 525°C was higher than that obtained after dehydration to only 350°C. Therefore, adsorption studies have been carried out with the Co(II) erionite samples after dehydration at the higher temperature of 525°C. It was found that adsorption of CO and ethylene onto 0.2 to 6-8 wt% Co(II) erionite zeolites significantly altered the optical spectra of the samples. The band at approximately 24,500 cm<sup>-1</sup> that is characteristic of bare Co(II) cations in six-ring window in zeolites disappeared upon adsorption of CO and ethylene, indicating that the Co(II) ions were accessible and underwent complexation by these reductant molecules. At the same time, the intensities of the spectra arising from the complexed Co(II) cations were more intense than those of the dehydration Co(II) centers. Therefore, there is no evidence that Co(II) was reduced by these weak ligands.

## TECHNICAL PROGRESS

The research during this quarter was centered on the influence of CO and ethylene adsorption on the optical spectra of Co(II) erionite zeolites that had been dehydrated at 525°C rather than the previously used lower temperature of 350°C [1]. Co(II) erionite samples containing 0.2, 1.7, 3.2, and 6-8 wt% Co(II) were prepared by aqueous ion exchange *via* single equilibrations with Co(II) solutions, usually using the acetate salt, of various molarities [2]. After exchange, the samples were filtered, washed three times with hot distilled water, and air-dried.

Dehydration of the samples was achieved by first heating to 350°C under dynamic vacuum (approximately  $7 \times 10^{-3}$  Torr) in a flask in three steps: 100°C for 1 hr, 220°C for 30 min, and 350°C for 3 hr. The heating ramp between these temperatures was 5°C/min. Samples were then heated to 525°C using a heating ramp of 10°C/min and maintained at this temperature for 8 hr. After dehydration, CO (99.0<sup>+</sup>% from Aldrich Chem. Co.) and ethylene (CP Grade from Linde) were adsorbed at ambient temperature. The CO was dried by the freeze/thaw technique using a trap of liquid nitrogen. The amount of gas adsorbed was controlled by adsorption at various pressures from volumes of 40, 180, or 1400 ml. Pressures of gases before and after adsorption were measured using a Pirani vacuum gauge. Adsorption was complete when no decrease in the pressure of the adsorbing gas was observed during a time interval of 15 min.

Diffuse reflectance spectra were obtained at ambient temperature using a computer-controlled Varian 2300 spectrophotometer with a MgO-coated integrating sphere. The

quartz sample cell contained a 24 mm diameter infrasil window for optical measurements. The spectra of the samples were transformed according to the Schuster-Kubelka-Munk theory using the relationship  $F(R_{\infty}) = (1-R_{\infty})^2/(2R_{\infty})$ , where  $R_{\infty}$  is the measured reflectance.

The spectra of the samples after dehydration at 525°C are shown in the VIS region of the optical spectrum in Figure 1. The 0.2 wt% Co(II) erionite exhibits one broad, weak band centered at about 25,000  $\text{cm}^{-1}$ , while the other three samples containing a higher level of Co(II) produce two bands having distinct shoulders. The bands are located at approximately 17,000 and 24,500  $\text{cm}^{-1}$ . These bands are similar to those observed for dehydration Co(II) A zeolite [3,4], which were assigned to the Co(II)  $d^7$  cation having approximately  $D_{3h}$  symmetry and located in the regular six-ring windows of the A zeolite structure [3]. Slight differences in the fine structure of the bands (the distinctiveness of the shoulders, especially the very distinct one at 19,000  $\text{cm}^{-1}$  for Co(II) A zeolite [4]) of Co(II) erionite as compared with Co(II) A zeolite might be explained by the small differences in the geometry of the six-rings in erionite (where all oxygens are located in the plane of the ring) and A zeolite (where oxygens are alternately located up and down from the plane of the ring) and by differences in aluminum distribution in the lattice ( $\text{Si/Al} = 3.5$  for erionite and  $\text{Si/Al} = 1$  for A zeolite).

To probe the accessibility to reductants and provide insight into the location (siting) of the Co(II) cations in erionite completely dehydrated at 525°C, adsorption of CO onto the samples was carried while monitoring the spectral changes by DRS. Figure 2 shows that the spectrum of the 3.2 wt% Co(II) erionite was significantly altered upon exposure to CO at ambient temperature. The band at about 24,500  $\text{cm}^{-1}$  is a characteristic peak for the bare

Co(II) cation with trigonal symmetry in dehydrated Co(II) zeolites. It is shown in Figure 2 that this band disappeared upon adsorption of CO onto the erionite sample. Therefore, all Co(II) cations in this sample were accessible for complexation by the weak CO ligand.

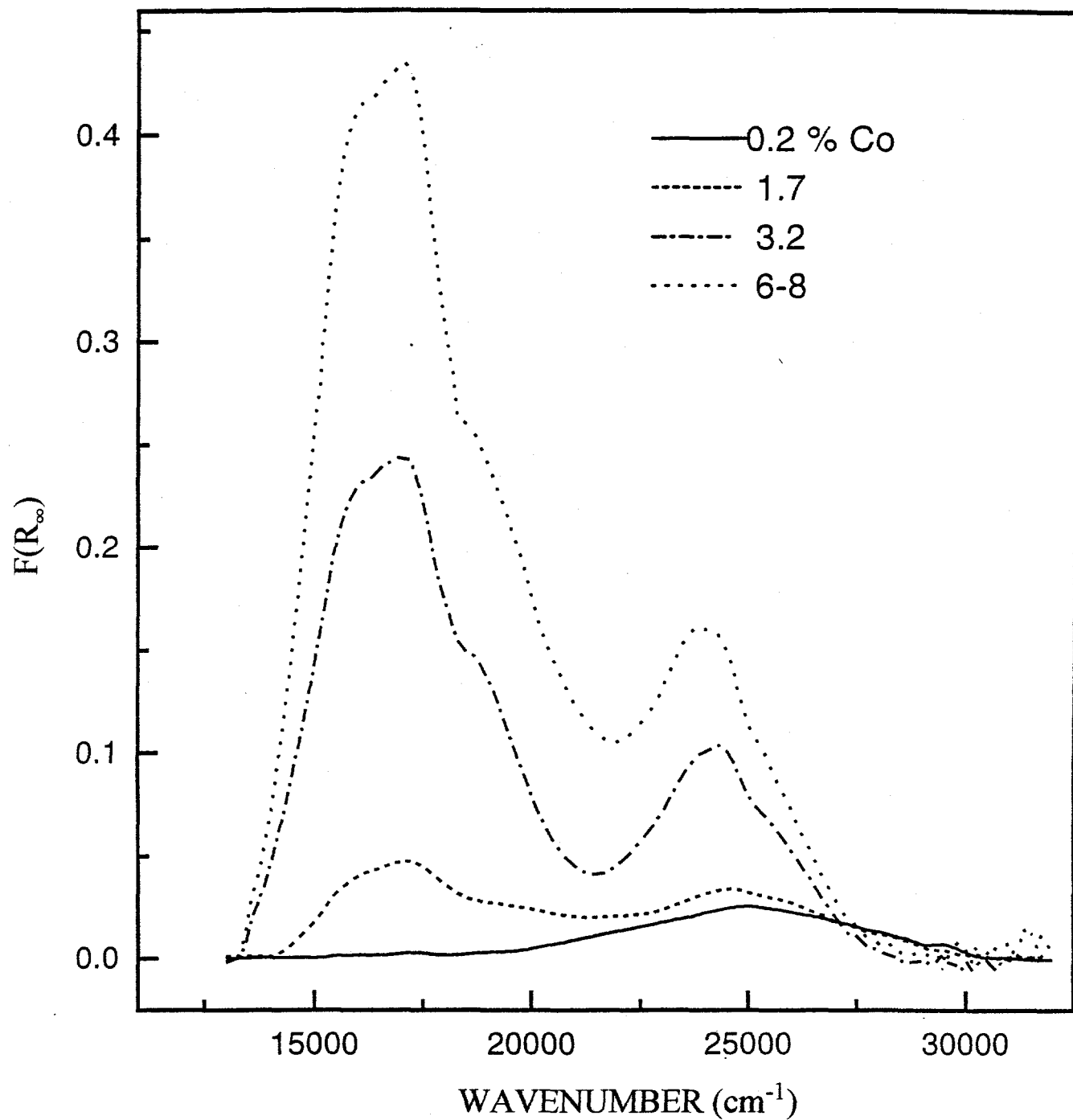
Similar adsorption experiments were carried out with ethylene as the adsorbate instead of CO. The observed change in the optical spectrum for the 1.7 wt% Co(II) zeolite upon adsorption of ethylene is shown in Figure 3. It is clear that the  $24,500\text{ cm}^{-1}$  nearly disappeared upon exposure to ethylene while the more intensity band at about  $17,000\text{ cm}^{-1}$  changed into three distinct bands located at approximately  $15,000$ ,  $17,500$ , and  $20,000\text{ cm}^{-1}$ , along with an apparent shoulder at about  $22,500\text{ cm}^{-1}$ . Carrying out a similar experiment with the 6-8 wt% Co(II) erionite led to very similar results, as shown by the spectra given in Figure 4. Therefore, all (or nearly all) Co(II) cations in six-ring windows in erionite are accessible to CO and ethylene ligands from the gas phase.

The adsorption experiments carried out this quarter, as monitored by DRS, demonstrate that the Co(II) cations in Co(II) erionite zeolites are accessible to and undergo complexation by reductant molecules, i.e. CO and ethylene, after dehydration at  $525^\circ\text{C}$ . The siting and accessibility of the Co(II) cations is expected to influence the activity of zeolite catalysts for the selective catalytic reduction (SCR) of NO by different reductants.

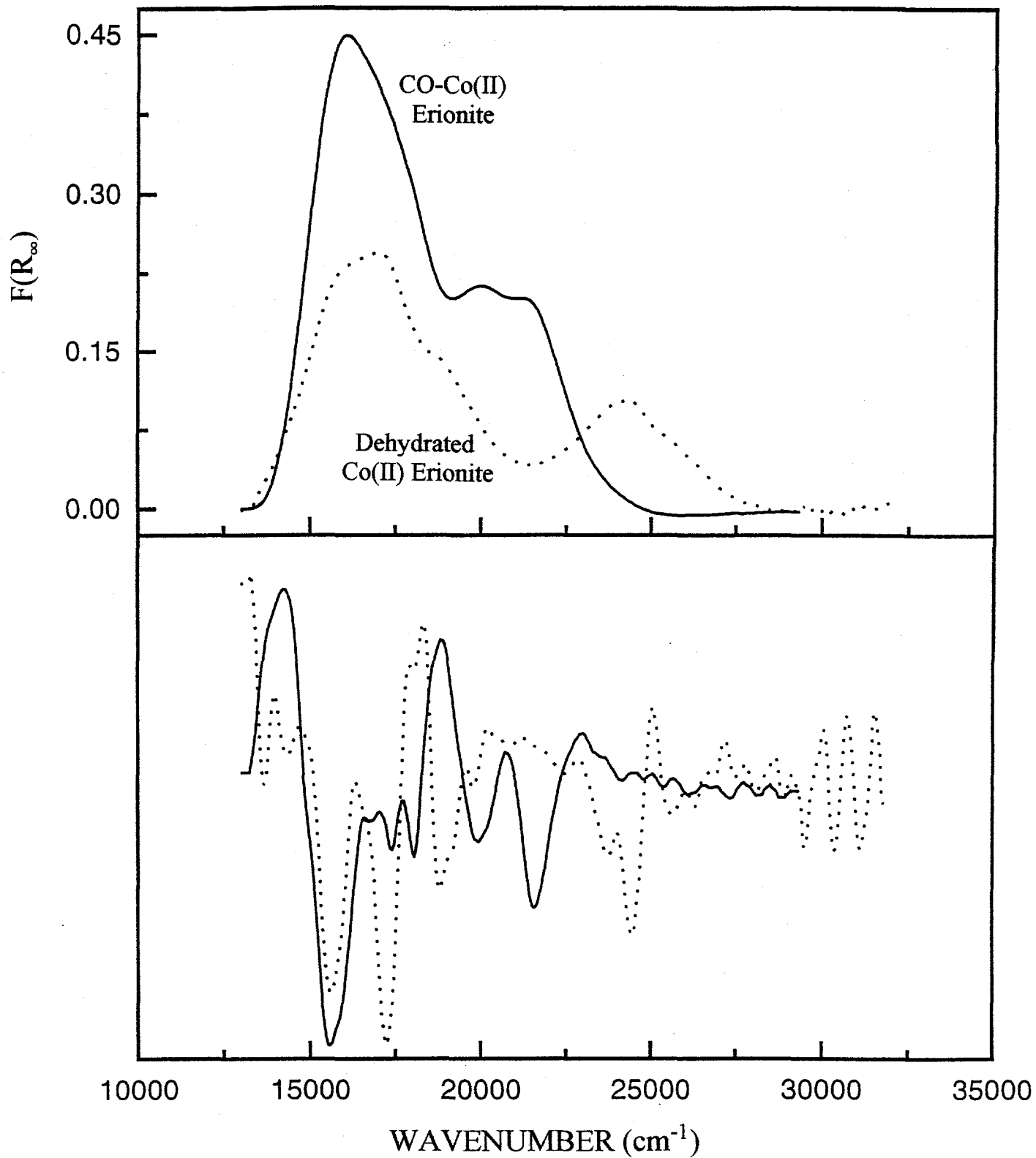
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4. Klier, K., Herman, R. G., and Hou, S., in "*Zeolites and Related Microporous Materials: State of the Art*," (Studies in Surface Science and Catalysis, Vol. 84), ed. By J. Weitkamp, H. G. Karge, H. Pfeifer, and W. Holderich, Elsevier, Amsterdam, 1507 (1994).

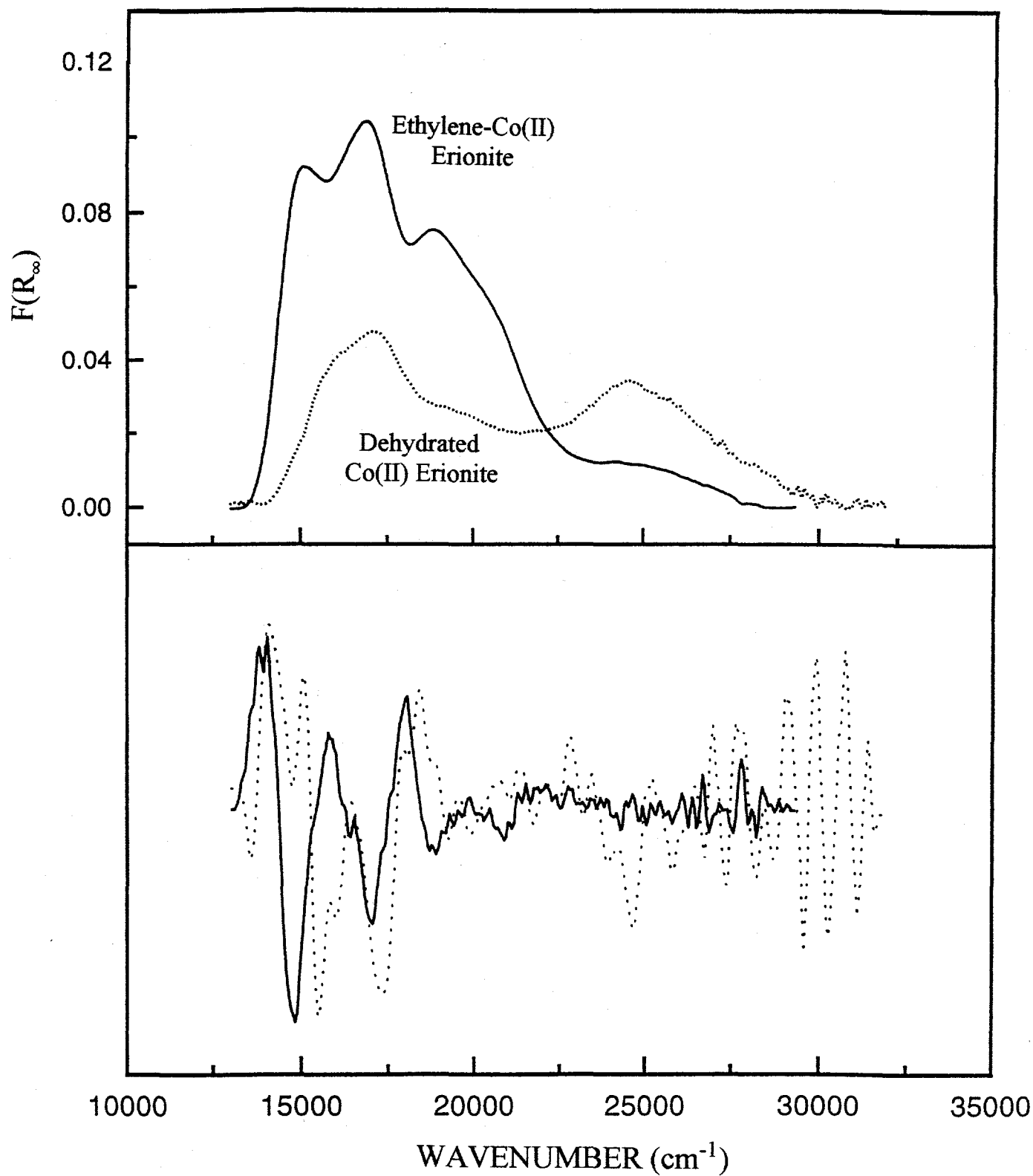




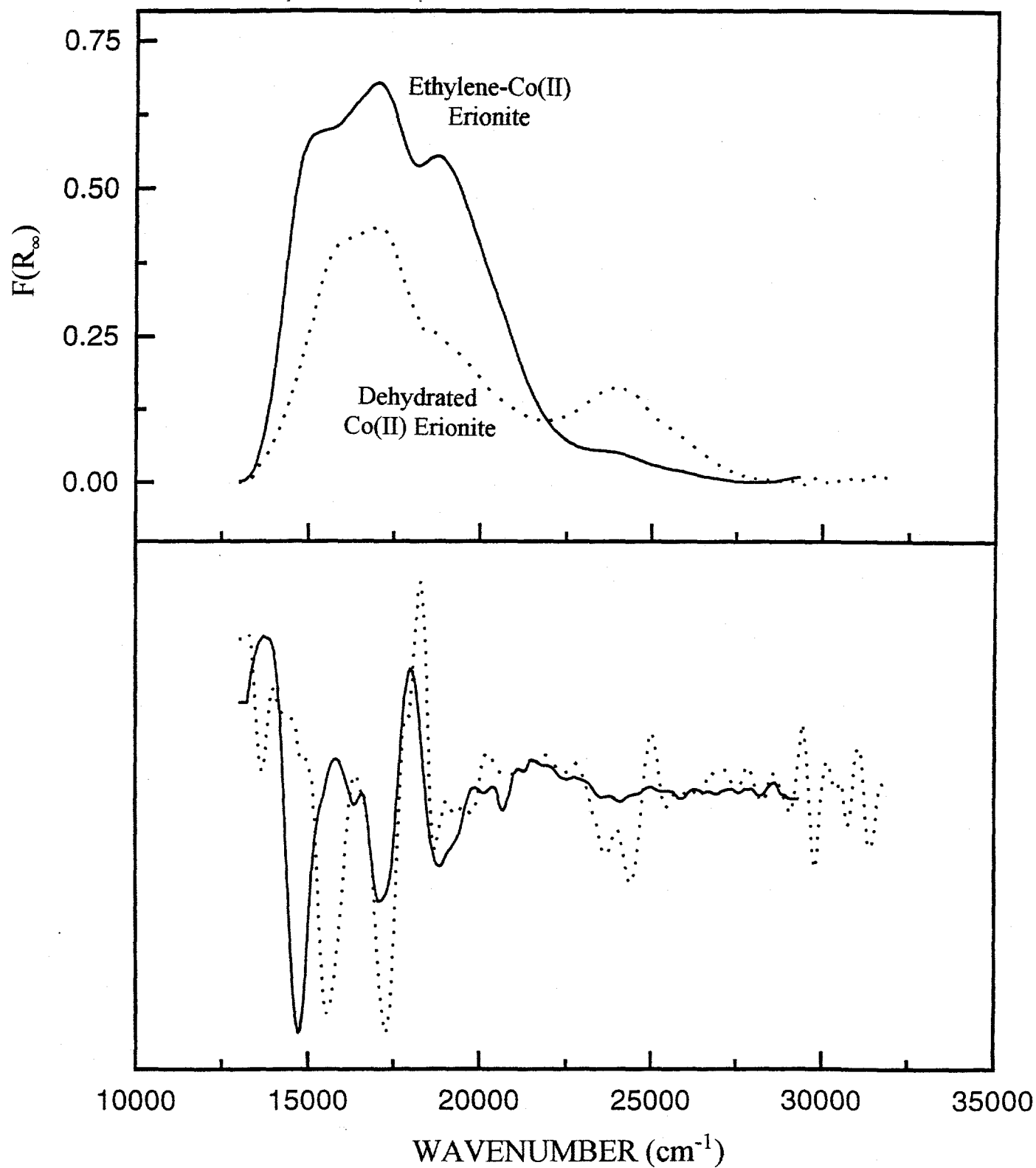
**FIGURE 1.** Diffuse reflectance spectra (VIS DRS) of Co(II) erionite samples containing different Co(II) contents (0.2 to 6-8 wt% Co(II)) dehydrated at 525°C.



**FIGURE 2.** Effect of CO adsorption (solid curve) on the VIS DRS of 3.2 wt% Co(II) erionite dehydrated at 525°C (dotted curve). Also shown is the comparison of the second derivative spectral curves.



**FIGURE 3.** Effect of ethylene adsorption (solid curve) on the VIS DRS of 1.7 wt% Co(II) erionite dehydrated at 525°C (dotted curve). Also shown is the comparison of the second derivative spectral curves.



**FIGURE 4.** Effect of ethylene adsorption (solid curve) on the VIS DRS of 6-8 wt% Co(II) erionite dehydrated at 525°C (dotted curve). Also shown is the comparison of the second derivative spectral curves.