DOE/PC/93222-7

NO DECOMPOSITION IN NON-REDUCING ATMOSPHERES

Technical Progress Report for the Period
March 1995-May 1995

Kamil Klier and Richard G. Herman

with

Jiří Dědeček

Zettlemoyer Center for Surface Studies
and Department of Chemistry
Lehigh University
Bethlehem, PA 18015

June 1995

PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY-Pittsburgh Energy Technology Center

Under Contract No. DE-FG22-93PC93222

U.S.-DOE Patent Clearance is not required prior to publication of this document.

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NO DECOMPOSITION IN NON-REDUCING ATMOSPHERES

SUMMARY OF TECHNICAL PROGRESS

Co(II) and Cu(II) ion exchanged samples of Nafion were prepared, and a Co(II)-ZSM-5 zeolite was obtained. All of these sample were studied by diffuse reflectance spectroscopy both in the hydrated state and after dehydration under a dynamic vacuum. It was shown that the Co-containing samples could be dehydrated under rather mild thermal conditions. The dehydrated samples give distinct spectra for the Co(II) ions. However, the Cu-Nafion sample was difficult to dehydrate while maintaining the stability of the Nafion matrix. NO adsorption and decomposition studies are being initiated with these samples.

TECHNICAL PROGRESS

The overall goal of this research is to establish the fundamental science needed to develop catalysts that will exhibit high activity and selectivity in the decomposition of NO into N_2 and O_2. This project is centered on the preparation, characterization, and testing of transition metal exchanged catalysts for NO decomposition, especially Co(II) zeolites. Additional metal ion exchanged catalysts have been prepared during this quarter. Of particular interest is the Co-ZSM-5 zeolite catalyst prepared. This will be tested for NO decomposition, and it will be fully characterized for comparison with Co A zeolites and with Cu zeolite catalysts. For further comparisons and insights into the state of the active metal sites in these catalysts, Co(II) Nafion and Cu(II) Nafion samples were also prepared. All of these materials were analyzed by optical diffuse reflectance spectroscopy to determine the state of the transition metal cations held in the catalysts before and after dehydration. The samples will be further analyzed by other techniques and will be used to study NO adsorption and decomposition.

Preparation and Optical Characterization of Co(II) Nafion

Nafion-H is a fluorocarbon sulfonic acid resin produced by duPont that is more thermally stable than are most other polystyrene-based sulfonic acid resins, e.g. the Amberlyst resins available from Rohm and Haas. The ion exchange capacity of the Nafion-H is 0.9 meq/g of resin. Two Co(II)-containing samples were prepared, wherein the Nafion-H resin was first completely exchanged with Na^+. In each case, 1.0 g of Na-Nafion was stirred for 3 h in 65 ml of $Co(NO_3)_2$ solution (0.04 M, pH = 3.0 or 0.16 M, pH = 1.9) at 80°C. After filtering, the exchanged Nafion was washed with hot water and air-dried. In both cases, it appeared that Co(II) completely replaced the Na^+ ions.

Optical diffuse reflectance analyses (UV-Vis-NIR DRS) were carried out with both samples. Optical spectra were obtained for the air-dried, but hydrated, samples, which were then dehydrated by dynamic evacuation at 140°C for 4 h or at 160°C for 2 h. The spectra for a dehydrated sample of Co-Nafion are shown in Figure 1 (UV-Vis) and Figure 2 (NIR). Complete dehydration of the Nafion upon thermal evacuation was indicated by the disappearance of NIR peaks corresponding to vibrational modes of the water molecule at 1900 and 1400 cm^{-1} and of OH at 1380 cm^{-1}. It was subsequently shown that the dehydration was reversible.

The NIR spectrum (Figure 2) and UV-Vis spectrum (Figure 1) showed bands centered at approximately 6,500, 17,000, and 24,000 cm^{-1}, which can be attributed to the Co(II) ions in the dehydrated Nafion. Additional fine structure bands are evident, and assignment of these will require further investigation. The band at 40,000 cm^{-1} is probably a charge transfer band, while the 47,000 cm^{-1} band corresponds to absorption by the Nafion matrix.

Optical Characterization of Co(II) ZSM-5 Zeolite

A sample of Co(II)-ZSM-5 zeolite prepared at Air Products and Chemicals, Inc. was obtained for optical characterization. This zeolite contained 4.4 wt% Co(II). Dehydration of this sample was carried out under dynamic vacuum at 195°C for 1 h, and DRS analysis in the NIR spectral region showed that complete dehydration had been achieved. The dehydrated sample was pale blue, and the spectra (Figures 3 and 4) exhibited bands centered at approximately 4,800, 6,500, 16,500, and 19,600 cm^{-1}. These spectral features for Co(II) were not observed for Co(II)-containing A, X, and Y zeolites.

Preparation and Optical Characterization of Cu(II) Nafion

A Cu(II)-Nafion sample was prepared for comparison with Cu(II)-ZSM-5 zeolite, which has been extensively studied by other for NO decomposition. This sample was prepared by equilibration of the Na-Nafion with a 0.01 M aqueous solution of $Cu(CH_3COO)_2$ at 65°C for 2 h. The sample was filtered and the equilibration was carried out a second time. After subsequent filtering, the sample was washed with hot water, air-dried, and then dehydrated under a dynamic vacuum at 140°C for 1 h. Samples that were subjected to dehydration at higher temperature or for longer evacuation times appeared to undergo degradation of the Nafion matrix.

The DRS spectrum of dehydrated Cu(II)-Nafion is shown in Figure 5. The sharp low intensity band at 5,200 cm^{-1} indicated that dehydration of the sample was not complete. Broad bands are evident at 12,500 and 35,000 cm^{-1}, with shoulders at ≈27,000 and ≈45,500 cm^{-1}. The band at ≈45,500 cm^{-1} is caused by Nafion matrix absorption.

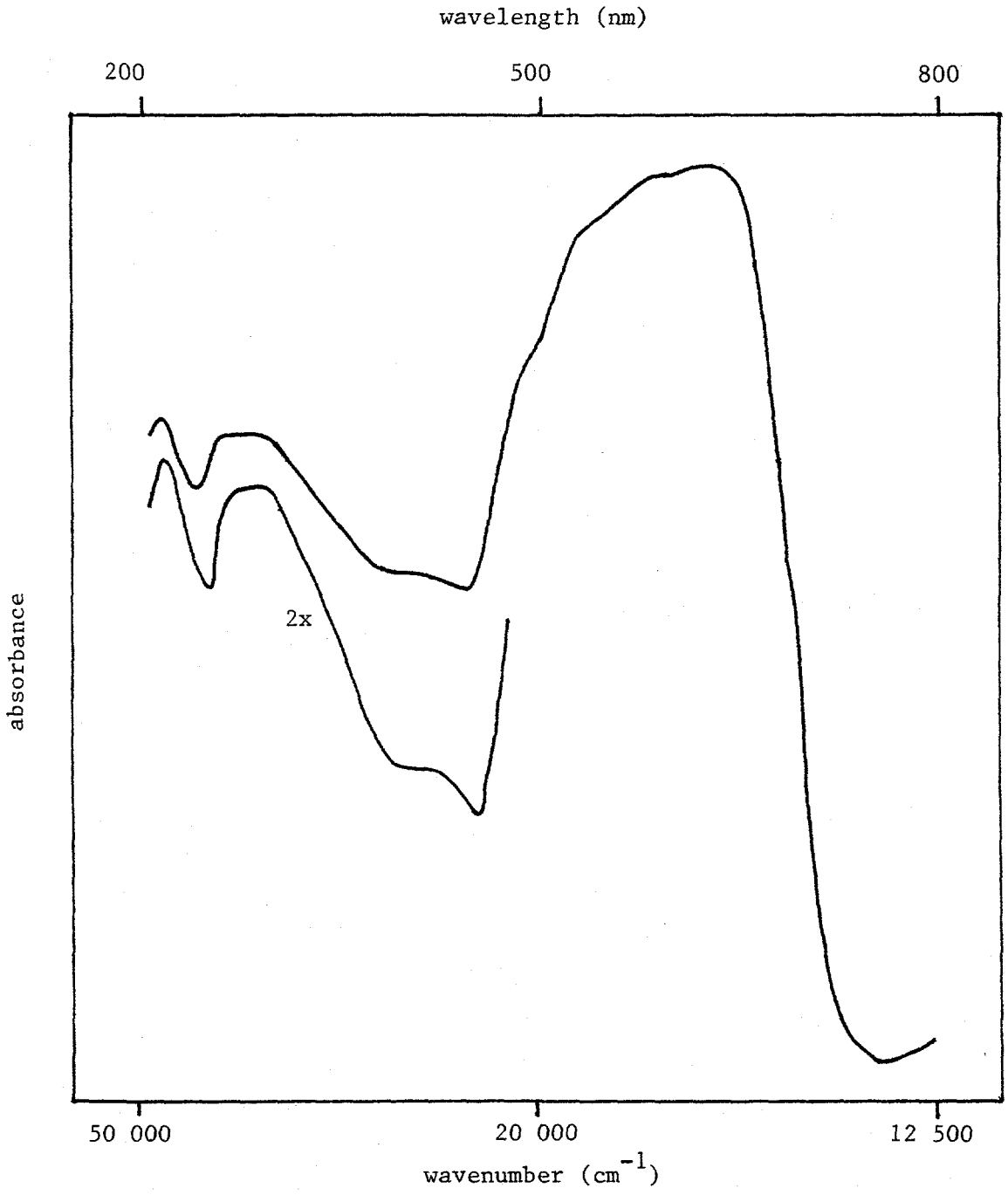

Figure 1

UV-VIS spectrum of dehydrated Co-nafion

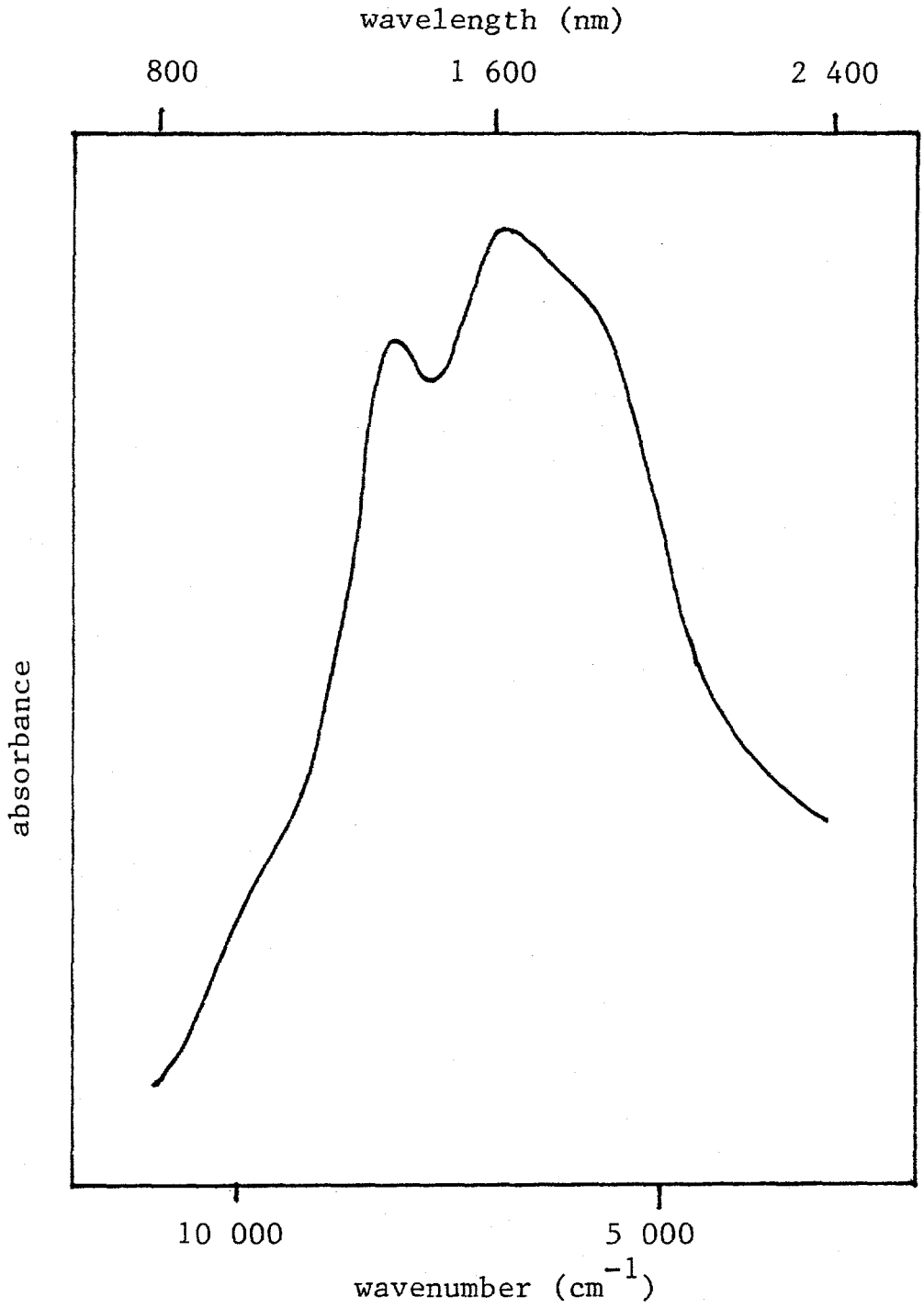

Figure 2

NIR spectrum of dehydrated Co-nafion

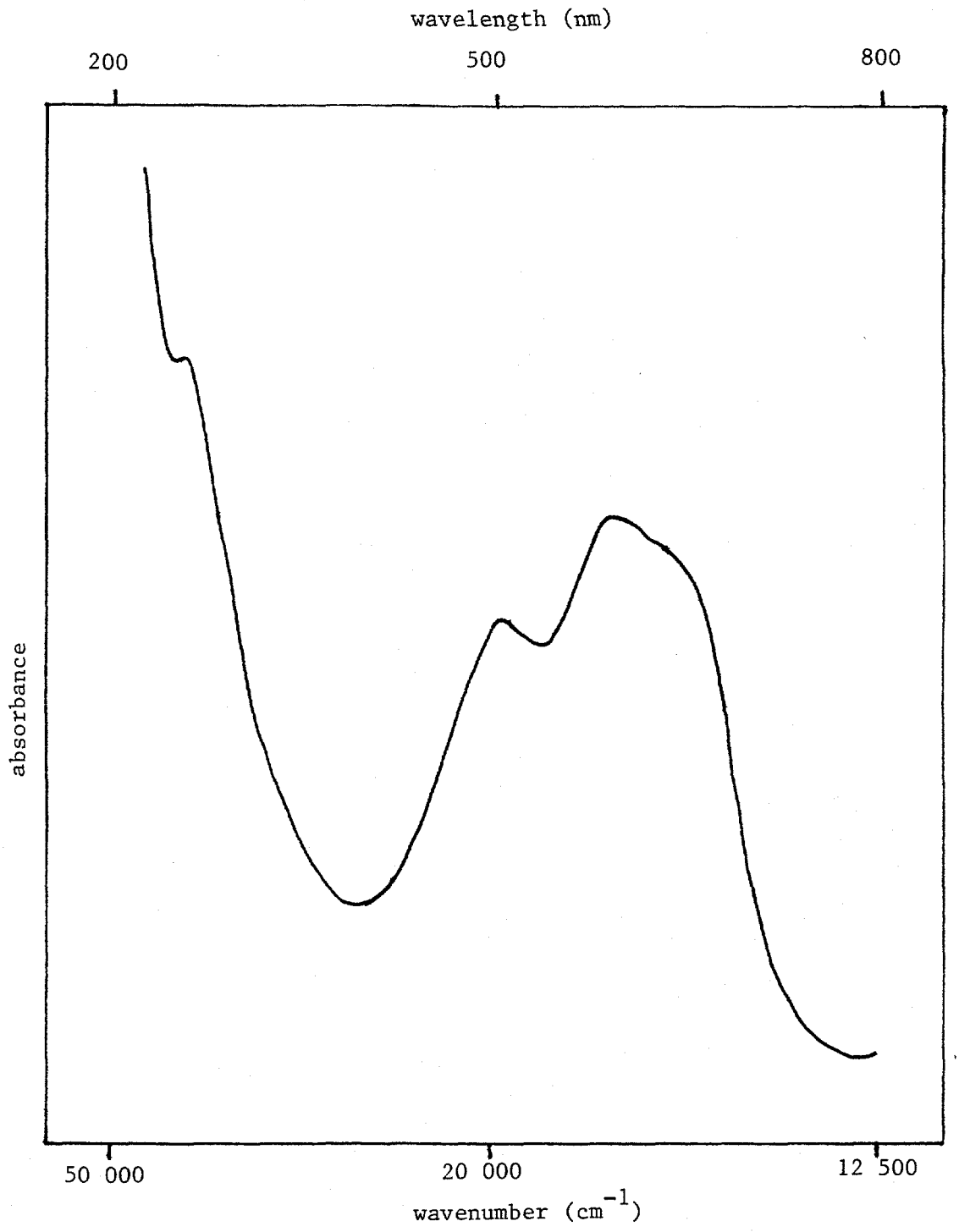

Figure 3
UV-VIS spectrum of dehydrated Co-ZSM-5

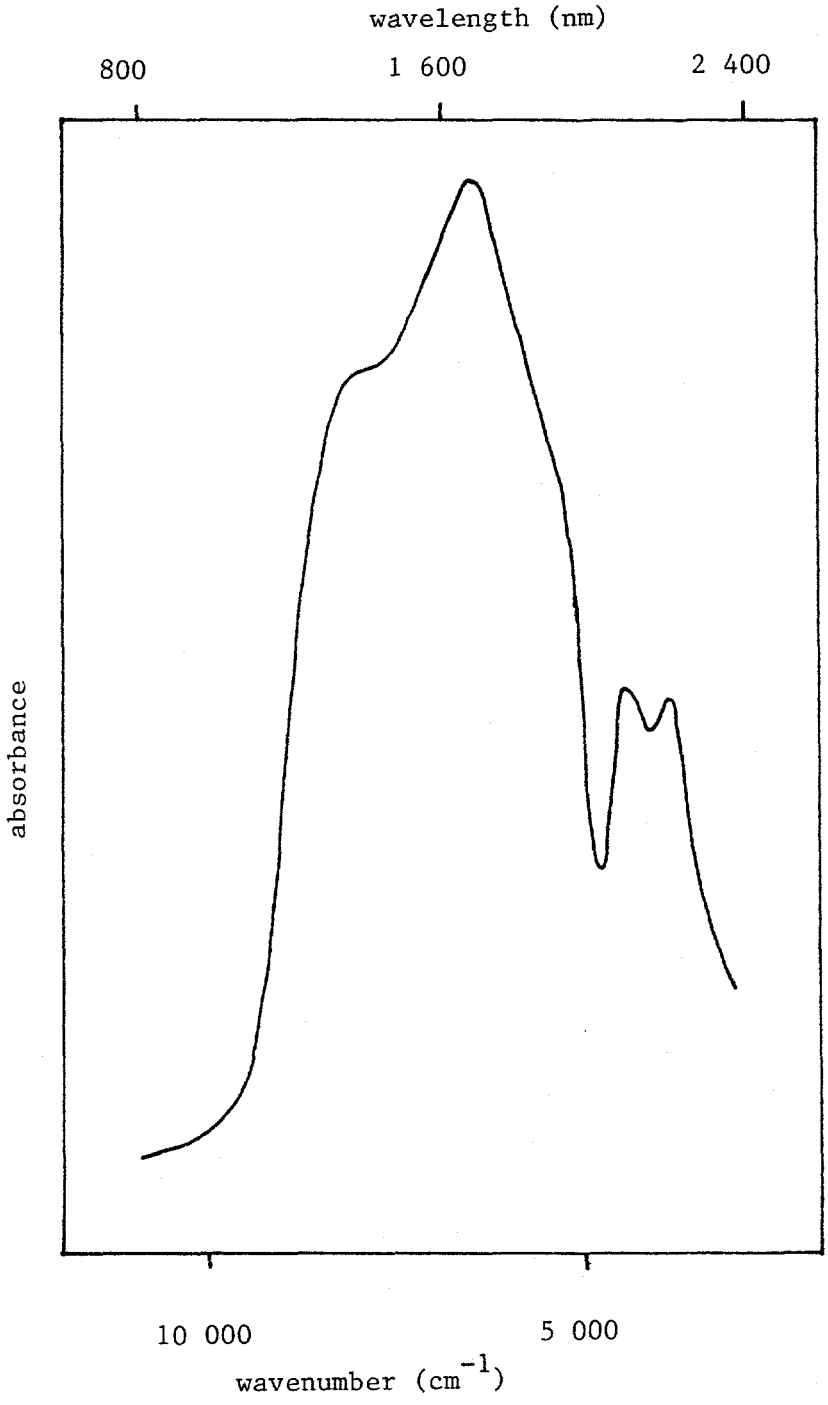

Figure 4

NIR spectrum of dehydrated Co-ZSM-5

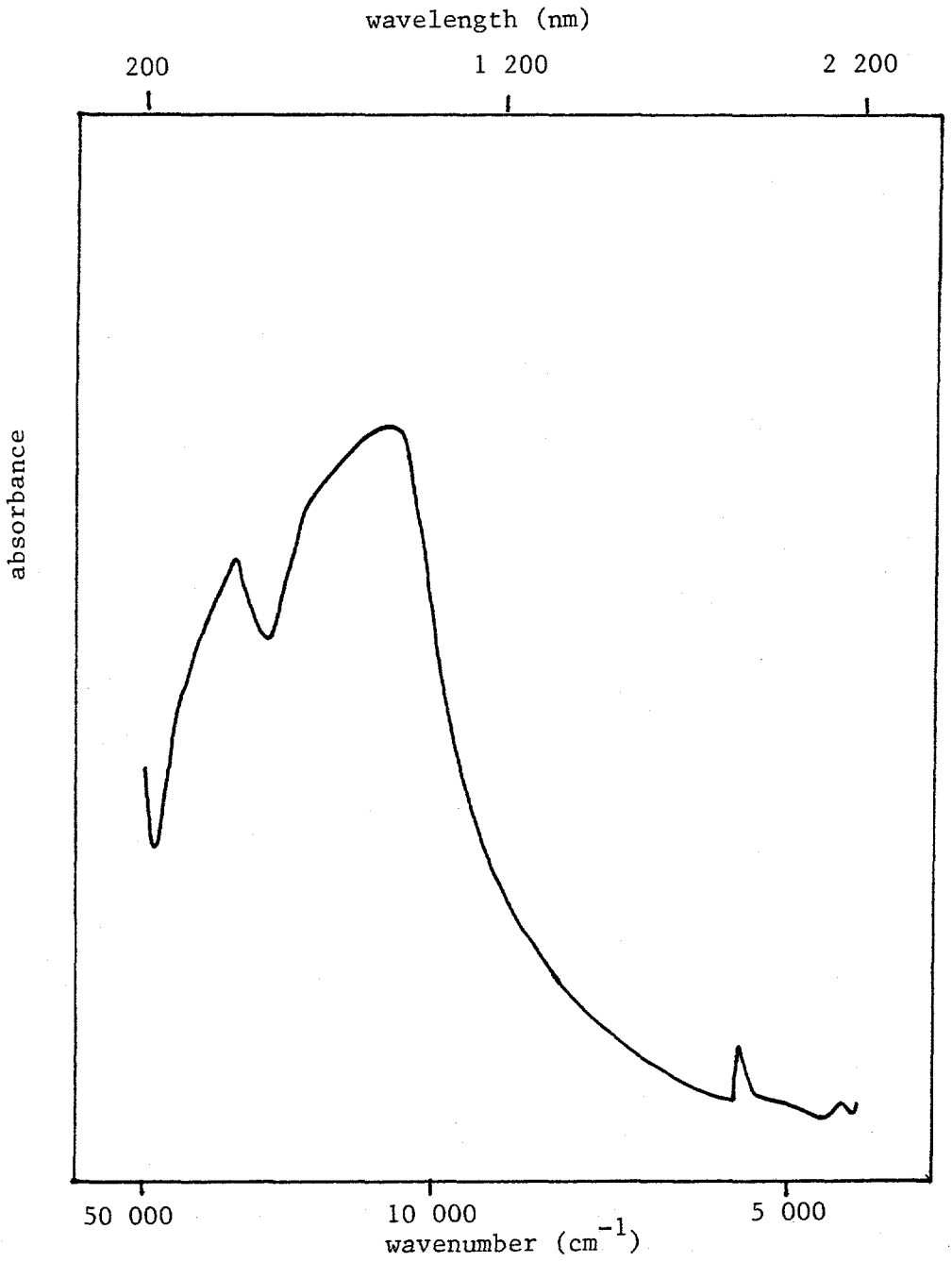

Figure 5

UV-VIS-NIR spectrum of dehydrated Cu-nafion