

INFRARED SPECTRA OF ADSORBED MOLECULES

by

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To Mother and Dad and to Kerin

## ABSTRACT

## INFRARED SPECTRA of ADSORBED MOLECULES

John Thomas Yates, Jr.

Submitted to the Department of Physical Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

The infrared spectrum of CO chemisorbed on Ni surfaces has been investigated in the region from  $1700\text{ cm}^{-1}$  to  $2400\text{ cm}^{-1}$ . The Ni is supported on a high area alumina powder. The full coverage spectra clearly show that the character of the Ni surface is a function of the Ni concentration. Ni surfaces ranging from a compact crystalline type to a dispersed type have been observed. Adsorption of CO on crystalline Ni sites occurs at very low pressures giving two surface species initially: a bridged CO between two adjacent Ni atoms, and a linear CO bonded to one surface Ni atom. At higher pressure a species formed by adsorption of a bridged CO between Ni atoms already having adsorbed linear CO species is proposed.

On more dispersed Ni sites CO is weakly adsorbed as a single linear species and the strength of adsorption decreases as the Ni atoms become less compactly arranged.

The relationship of Hg poisoning of a Ni surface to the chemisorption of CO has been investigated.

Thesis Supervisor: Carl W. Garland  
Title: Associate Professor of Chemistry

## ACKNOWLEDGEMENT

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Mr. K.A. Loftman, Godfrey Cabot Inc., White Pigments Division, 77 Franklin St., Boston 10, Mass., supplied us with a generous amount of Alon C.

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Mr. Ronald Chandross instructed the author in the use of equipment in the X-ray laboratory.

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Prof. R.C. Lord has commented on the early phases of this work and has allowed the author to use the facilities within the Spectroscopy Laboratory.

Special thanks are due to Prof. C.W. Garland who always has found time to comment constructively on the problems encountered. The author would also like to thank Prof. Garland for the rewarding relationship which he has had with him throughout four years at M.I.T.

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## I. INTRODUCTION

### A. Physical Adsorption and Chemisorption

Gas-solid adsorption phenomena are generally divided into two broad categories - physical adsorption and chemisorption. Physical adsorption is of general occurrence; the forces involved are of the van der Waals type and for this reason physical adsorption of gases occurs at temperatures not too far above their normal boiling points. Thus, this type of adsorption may be regarded as being essentially a preferential condensation of a vapor on a surface. Multilayer formation is common and the formation of multilayers proceeds in the limit to bulk condensation of the adsorbate. Thus physical adsorption may be regarded as a continuous transition from an initial situation where a molecule adsorbed on a surface is unaffected by neighbors of its own kind to the final situation where bulk condensation occurs. Van der Waals interactions are of a quite general nature; therefore physical adsorption is fairly nonspecific and the adsorbed molecules are not localized relative to a given adsorbent atom. The layer of physically adsorbed molecules is similar to a liquid-like film.

Adsorption processes always involve a negative entropy change and are therefore always exothermic. The heat liberated in physical adsorption is of the order of 5 - 10 kcal. per mole or less.

Volumetric or gravimetric measurements of the physical adsorption of a gas make possible an estimation of

the total surface area of a finely divided solid. Studies of the hysteresis of adsorption - desorption isotherms give information related to the thermodynamically irreversible condensation of adsorbate molecules in capillary pores of the solid adsorbent.

From calorimetric studies of the heat liberated in physical adsorption processes it is possible to deduce the nature of interactions between physically adsorbed molecules. Generally the heat of adsorption drops off as coverage increases. Determination of the adsorption isotherms at various temperatures also allows an estimate to be made of the heat of adsorption as a function of coverage.

Chemisorption is an entirely different phenomenon. The best criterion for deciding whether a particular adsorption process is classed as chemisorption involves knowing whether sharing or exchange of electrons takes place between the adsorbate and adsorbent. Thus chemisorption involves the formation of a chemical bond, and the heat effect at low coverage will be comparable in magnitude to bond energies in chemical compounds. Because of the specific interaction of an adsorbed molecule with a surface atom, multilayer formation does not occur in chemisorption. It is possible, however, to physically adsorb molecules on top of a layer of chemisorbed molecules.

Many diversified experimental techniques have been employed to study adsorption. Isotherm measurement and calorimetric studies have already been mentioned. Recently

measurements of changes in the electrical conductivity of metal oxide films during adsorption have contributed to the understanding of electronic factors in adsorption.<sup>1</sup> Studies of work function changes during adsorption give information about the nature of surface dipoles. Also, the mobility of chemisorbed atoms and molecules has been investigated through the use of the field emission microscope.<sup>34</sup> Finally, chemical studies of catalytic reactions have contributed to a better understanding of surface phenomena. Indeed, almost every investigation of adsorption phenomena is motivated to a large degree by a desire to understand catalysis.

#### B. Electronic Factors in Chemisorption

Very little direct evidence concerning the nature of the bonding between adsorbed gas molecules and transition metal adsorbents is available. The ability of the transition metals to act as chemisorbers is ascribed to the presence of the unfilled d shell in the metal and the interaction of the electrons of the adsorbate with this partly filled shell. Experimental evidence for this type of bonding process is available in magnetic susceptibility studies which show that as chemisorption takes place the paramagnetic susceptibility of the catalyst decreases as electrons from the adsorbate are paired with adsorbent electrons.

Pauling<sup>2</sup> has proposed a theory of metals which involves three types of hybrid d orbitals: (a) bonding d orbitals which resonate among the nearest neighbors of a given metal atom in forming the crystalline lattice; (b) atomic d

orbitals which are not used in metal-metal bonds; (c) "metallic" d orbitals which may contain conduction electrons.

Chemisorption may be visualized as an overlap of the orbitals for some of the electrons of the adsorbate with atomic d orbitals of the adsorbent.<sup>3</sup>

Nickel metal has 10 electrons outside its argon-like core. Pauling considers nickel to have a resonating electronic configuration composed of two structures designated as:

	3d	4s	4p
Ni A	↑↓ ↑ ↑ . .	.	. . .
Ni B	↑↓ ↑↓ . . .	.	. . ○

Here the dots represent bonding d orbitals; the arrows represent the electron spins in atomic orbitals; the open circle represents an empty "metallic orbital". Magnetic susceptibility measurements on Ni lead to the postulate that A contributes 30% and B 70% to the resonance structure thereby giving a saturation moment of 0.61 Bohr magnetons.

The electronic situation within a metal catalyst may be altered by alloying the metal catalyst with various proportions of another metal. Thus Cu-Ni alloys have been investigated as catalysts for the hydrogenation of benzene<sup>4</sup> and ethylene.<sup>5</sup> The mechanism for hydrogenation is probably different in these two compounds but in both cases it is found that the catalytic activity of the alloys is a function of the alloy composition.

C. Infrared Studies of Carbon Monoxide Chemisorbed on Nickel

None of the methods previously described for studying adsorption is able to give direct information about the molecular configuration of adsorbed species. In 1954 Eischens and coworkers published studies of chemisorbed species using infrared spectroscopy.<sup>6,7</sup> This method is reported to have been applied previously by Terenin in Russia to studies of chemisorbed NO.<sup>8,9,10</sup> Other studies of chemisorbed molecules have been made by Little who studied in detail the chemisorption of ethylene by oxides of Ni, Cu, and Pd.<sup>11</sup>

Yang and Garland have studied the chemisorption of CO by Rh<sup>12</sup> and Garland has reported the effect of CS<sub>2</sub> poisoning on CO chemisorption by supported Ni surfaces.<sup>13</sup> Recently studies of infrared reflectance spectra of metal films containing chemisorbed molecules have been reported.<sup>14</sup>

Eischens has studied the decomposition of formic acid by Ni catalysts using the infrared technique to observe intermediate molecular species.<sup>15</sup> Infrared spectroscopy applied to surface chemistry has been reviewed by Eischens<sup>16</sup> and also by Sheppard.<sup>17</sup>

The work to be described herein deals with a more extensive infrared study of chemisorbed CO on alumina - supported Ni. Carbon monoxide gas has a small dipole moment ( $\mu = 0.11$  debye) and its fundamental infrared adsorption band is at  $2143 \text{ cm}^{-1}$ . When CO is chemisorbed by Ni the intensity

of the fundamental CO stretching vibration increases manyfold and the frequency is lowered. The lowering of the frequency is indicative of a decrease in the bond order for the carbon - oxygen bond upon chemisorption. The higher intensity of infrared absorption is related to a corresponding increase in  $(\frac{d\mu}{dQ})^2$  for the adsorbed species, where Q is the normal coordinate for the carbon - oxygen stretching vibration.<sup>18</sup>

## II. EXPERIMENTAL

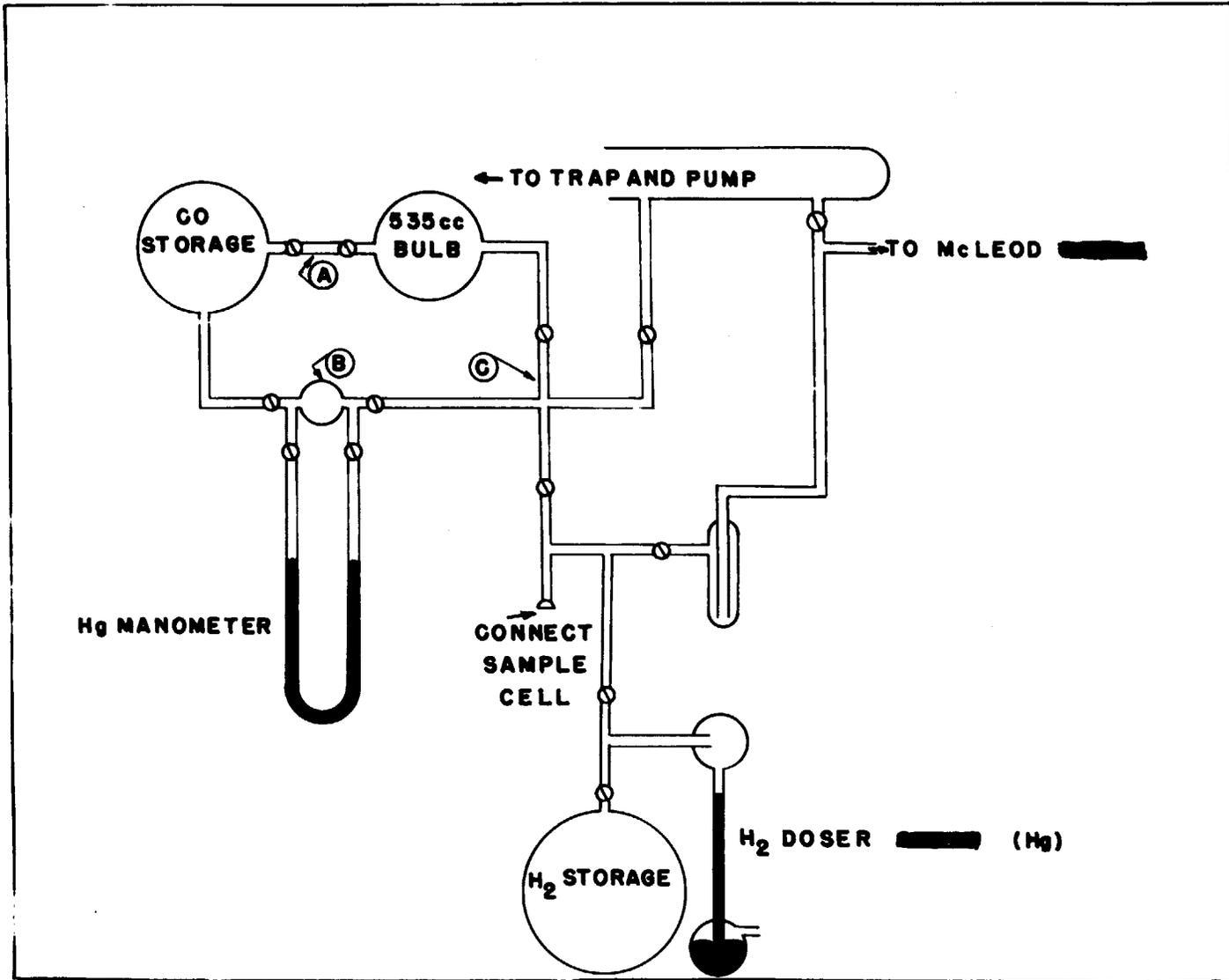
### A. Vacuum System

An all-glass vacuum system was designed to prepare samples for adsorption and to measure adsorption isotherms. The system is evacuated with a Langmuir type mercury diffusion pump backed by a Cenco-Hyvac 2 oil pump. The pumping stage is connected to the vacuum system through a liquid nitrogen trap. The diffusion pump and the nitrogen trap may be bypassed by a line which connects the Cenco-Hyvac 2 oil pump directly to the vacuum system. The system is capable of maintaining a vacuum of  $1 \times 10^{-6}$  mm.

The gas-handling portion of the system is shown in Figure I. The CO storage bulb contains Matheson chemically pure carbon monoxide (min. 99.5% CO) at about one atmosphere pressure as measured on the Hg manometer. Ordinarily, carbon monoxide at this pressure is expanded into section A ( $1.78 \text{ cm}^3$ ) and then this slug is expanded into the  $535 \text{ cm}^3$  bulb. A small fraction of the gas in this expansion bulb may be added to the sample cell by expansion into section C ( $7.43 \text{ cm}^3$ ) or section C plus B ( $7.43 \text{ cm}^3 + 23.7 \text{ cm}^3$ ). Occasionally it is necessary to add larger quantities of carbon monoxide to the sample cell and this is accomplished by expanding directly from the storage bulb into section B.

The vacuum system contains a hydrogen dosing section which is used to add reproducible quantities of  $\text{H}_2$  to the samples during reduction. The five liter hydrogen storage bulb is filled to a pressure of about one atmosphere with

**Figure I Vacuum System**



Airco regular grade hydrogen (max. 0.5% O<sub>2</sub>). Hydrogen is admitted to the bulb at the top of the barometric doser gauge and then this gas is expanded into the sample cell. The final hydrogen pressure in the sample cell can be obtained by the difference in the Hg column height before and after hydrogen addition to the cell.

A large (500 cm<sup>3</sup>) McLeod gauge is connected to the vacuum system through a small liquid nitrogen trap. The McLeod gauge is also directly connected into the vacuum manifold. With this gauge it is possible to measure pressures in the cell within the range of  $1 \times 10^{-6}$  to  $6 \times 10^{-2}$  mm. Using calibration data obtained by Dr. A.C. Yang when the McLeod gauge was constructed,

$$P_{\text{mm}} = 1.439 \times 10^{-6} \times \Delta h^2 \text{ mm}$$

for this gauge.

#### B. Infrared Cell

The infrared cell has been described in detail previously.<sup>12</sup> Briefly it is a pyrex cylinder, 180 mm in length, with a volume of 150 cm<sup>3</sup>, assembled from a large (40/35) standard taper joint and has circular CaF<sub>2</sub> windows sealed on each end with glyptal. A side arm with a vacuum stopcock and a spherical ball joint permits the cell to be removed from the vacuum system. The central portion of the cell is wrapped with a heating wire and asbestos, and in this section the sample is supported on a 30 mm diameter CaF<sub>2</sub> plate which completely occupies the circular cross section. The greased

taper joint is cooled from the outside with a detachable helical copper cooling coil. The cell is maintained in a vertical position during all operations.

The cell heater was calibrated using a chromel-alumel thermocouple which touched the center of the  $\text{CaF}_2$  sample plate. Actual reduction of the samples was carried out in the cell without this thermocouple since it was found that the seal around the entering thermocouple wires could not easily be made vacuum tight.

### C. Infrared Spectrometer

The infrared spectrometer used for this work has also been described previously.<sup>12</sup> It is a single beam Perkin Elmer model 12 instrument which has been modified by adding an external chopped source and vertical source optics. This arrangement accommodates the vertical sample cell. The entire spectrometer may be flushed with nitrogen to remove interfering infrared absorption bands of atmospheric water vapor and carbon dioxide. The spectrum is recorded on a Brown strip chart recorder driven at 1.5 inches per minute. The scanning rate is about  $16 \text{ cm}^{-1}$  per minute in the  $2000 \text{ cm}^{-1}$  range.

All of the spectra reported have been obtained with a  $\text{CaF}_2$  prism in combination with a 150 lines/mm grating, blazed at 4.5 microns in the first order. This grating is mounted in the Littrow mirror position. A Kodak 230 filter (40% transmission at 5 microns, opaque at 3 microns) was placed over the exit slit to remove higher orders of the grating. With this arrangement, larger slit widths than those

employed with a prism alone can be used with no sacrifice in resolution. Thus studies of weaker bands using thicker samples become feasible as a result of the higher energy made available by larger slit widths. Also, small shifts in the frequency of the infrared absorption bands are more easily observed as a result of the increased dispersion obtained with this arrangement. Spectra taken under the most unfavorable conditions, i.e. at the highest gain settings, exhibit a signal to noise ratio of about 30:1. Most of the spectra have been recorded under conditions of noise more favorable than this.

#### D. Sample Preparation

Supported nickel surfaces have been prepared by a novel spraying technique. The support used was Alon C, a high area non-porous alumina obtained from Godfrey Cabot Inc. The Alon C used in this work consists of particles about 0.015 microns in diameter with a specific surface area of 90 m<sup>2</sup> per g. It is transparent in the spectral region investigated, 1700 cm<sup>-1</sup> - 2400 cm<sup>-1</sup>.

Alumina supported nickel surfaces in the concentration range 1.5% - 25% Ni have been investigated. The samples are prepared as follows: A weighed amount of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Mallinckrodt A.R. grade, is dissolved in a small volume of distilled water. Reagent grade acetone is added to the solution and a weighed amount of Alon C is added with shaking. The final slurry contains about 4 g Alon C per 100 cm<sup>3</sup> of solution and the acetone-water solution is between

20 and 22% distilled water by volume. The resulting slurry is allowed to stand a few minutes with shaking and is then transferred to a special mixing reservoir. Here the slurry is continuously mixed by means of a stream of bubbles while a portion is continuously withdrawn through a capillary into an atomizer. The fine spray produced is directed toward several weighed circular 30 mm diameter  $\text{CaF}_2$  plates which are heated to 60 - 80°C on a micro-hot plate. A uniform coherent deposit is produced and there is little tendency toward cracking of the deposits. The pressure of the carrying gas is adjusted so that most of the evaporation of water and acetone occurs within the cone of spray before it reaches the heated  $\text{CaF}_2$  plates. Thus there is no tendency for the sample to become visibly wet during the spraying operation. About 10% of the total weight of Alon C used to make the slurry actually is deposited on the plates (when three plates are sprayed simultaneously). The majority of the spray is spread over the area surrounding the  $\text{CaF}_2$  plates due to the large solid angle of the spray. The weight of the Ni-alumina deposits used in this work ranges from about 13 mg/cm<sup>2</sup> to 53 mg/cm<sup>2</sup> after reduction.

The sample plate is then transferred to the infrared cell and the cell is assembled. Dow-Corning high vacuum silicone grease is used to seal the large standard taper joint. The cell is connected to the vacuum system by means of the greased ball and socket ground joint. The following procedure for drying and reduction is carried out.

Table I

OPERATION	TEMPERATURE	TIME	PRESSURE
(1) rough pump	25°C	1/2 hr.	$\sim 1 \times 10^{-3}$ mm
(2) rough pump	150°C	1 hr.	$\sim 1 \times 10^{-3}$ mm
(3) Hg pump	300°C	1/2 hr.	$\sim 3 \times 10^{-4}$ mm
(4) H <sub>2</sub> reduction	300°C	1 hr.	$\sim 150$ mm H <sub>2</sub>
(5) rough pump	300°C	1/4 hr.	$\sim 1 \times 10^{-3}$ mm
(6) H <sub>2</sub> reduction	300°C	1-3 hr.	$\sim 150$ mm H <sub>2</sub>
(7) Hg pump	300°C	2 hr.	$\sim 1 \times 10^{-4}$ mm
(8) H <sub>2</sub> reduction	300°C	12-18 hr.	$\sim 150$ mm H <sub>2</sub>
(9) Hg pump	300°C	3 hr.	$\sim 2 \times 10^{-5}$ mm
(10) Hg pump	300°C-25°C	1/2 hr.	$\sim 1 \times 10^{-6}$ mm at 25°C

After the last preparative step has been carried out, the cell is placed into the spectrometer and a background spectrum is recorded over the spectral region of interest. The spectra reported herein have been plotted as absorbance values,  $-\ln I/I_0$ , where  $I_0$  is the recorder deflection from 0% transmission to the background curve, and  $I$  is the deflection from 0% transmission to the spectral curve produced by adsorption of CO.

#### E. Special Experimental Techniques

1. In some cases it was desired to expose a sample to Ni(CO)<sub>4</sub> gas. A sample of Ni(CO)<sub>4</sub> was obtained in a sealed ampoule from Prof. F.A. Cotton, M.I.T. Department of Chemistry. It was transferred to a bulb equipped with a vacuum stopcock and a ball joint. This bulb was attached to

the vacuum system and the  $\text{Ni}(\text{CO})_4$  liquid was thoroughly degassed by successive cycles of freezing at  $77^\circ\text{K}$ , pumping, and warming to room temperature. After several cycles, a portion of the  $\text{Ni}(\text{CO})_4$  was distilled into a  $50\text{ cm}^3$  cold finger immersed in liquid nitrogen. This cold finger was equipped with a vacuum stopcock and a ball joint through which it is attached into the vacuum system. This cold finger was subsequently immersed in an ice bath and  $\text{Ni}(\text{CO})_4$  gas was expanded into the various calibrated sections of the vacuum system as needed. At  $0^\circ\text{C}$  the vapor pressure of  $\text{Ni}(\text{CO})_4$  liquid is  $133.7\text{ mm}$ .<sup>19</sup> Small known fractions of the  $\text{Ni}(\text{CO})_4$  gas could be expanded into the cell by successive expansion from section to section.

2. A better method than successive expansion for adding accurately known quantities of  $\text{Ni}(\text{CO})_4$  gas to a sample involved the use of a capillary doser of known volume connected between a cold finger containing  $\text{Ni}(\text{CO})_4$  liquid at  $0^\circ\text{C}$ , and the sample cell. Connected into this particular system is a thermocouple gauge in series with two expansion sections of known volume. This arrangement allowed measurements of CO pressure to be made in a system of known dead-space volume after each addition of  $\text{Ni}(\text{CO})_4$  gas to the sample cell.

3. Hg vapor was accidentally found to cause changes in the spectrum of CO adsorbed on Ni samples. In order to investigate this effect it was necessary in later stages of the work to add Hg vapor from a dosing apparatus. Because of the

low vapor pressure of Hg at room temperature, it was possible to make a clean droplet of Hg be the source of the vapor. Hg could then be added to the cell at different pressures by controlling the temperature of the droplet which was contained within a finger in the vacuum system. In further experiments it was decided that the best reproducible source of Hg in successive experiments would be in each case a freshly prepared Hg surface. A doser was constructed in such a fashion that Hg could be sublimed in vacuo from a reservoir into a section cooled with liquid nitrogen. Upon removing the liquid nitrogen, the Hg mirror formed by the sublimation coalesced into visible droplets, presumably with clean surface. This Hg was used as a source of the vapor, and two successive experiments carried out for the same length of time showed a quantitative correspondence in the magnitude of the observed Hg poisoning effect.

### III. RESULTS

Small variations in the full coverage spectra were common throughout this work due to the difficulty in preparing identical surfaces in different samples. Thus, some of the spectra shown have been selected to represent behavior which is typical of that observed in replicate experiments. Altogether the information reported herein has been selected from over five hundred spectra which represent about forty samples.

It is convenient for discussion to divide the spectral region investigated into five overlapping frequency regions. These frequency regions are as follows:

Table II

REGION	APPROXIMATE FULL COVERAGE BAND CENTER	FREQUENCY RANGE
A	1915 $\text{cm}^{-1}$	1850 - 1960 $\text{cm}^{-1}$
B	1963 $\text{cm}^{-1}$	1930 - 1990 $\text{cm}^{-1}$
C	2035 $\text{cm}^{-1}$	1990 - 2065 $\text{cm}^{-1}$
D	2057 $\text{cm}^{-1}$	2050 - 2110 $\text{cm}^{-1}$
E	2082 $\text{cm}^{-1}$	2060 - 2140 $\text{cm}^{-1}$

#### A. Stepwise Addition of CO to 10% Ni Samples

Measured amounts of CO were added to the samples and equilibrium was considered to be established when successive pressure readings on the McLeod gauge were constant over 5 - 10 minute intervals. It was observed that the equilibrium condition was obtained rapidly at low pressures while at higher

coverages the pressure tended to become constant more slowly ( $\sim 1$  hr.). Due to the slow attainment of equilibrium the higher pressures measured are probably larger than the true equilibrium pressure.

A series of typical isotherms observed for 10% Ni samples is shown in Figure II. The various pressure ranges designated on the isotherms correspond qualitatively to the stages in adsorption where distinct infrared absorption bands appear as designated in Table II. The isotherms show that on 10% Ni samples the total uptake of CO per unit weight of Ni may vary as much as 50% from sample to sample even though preparation conditions were similar on all samples. The isotherms show that on a 10% Ni sample equilibrated at about  $5 \times 10^{-2}$  mm CO pressure, about 1 Ni atom in 20 is involved in chemisorption at room temperature (assuming each active Ni atom adsorbs only one CO molecule).

Figure III shows the growth of bands for increasing coverage of CO on a typical 10% sample. Initially at the lowest coverage ( $p < 1 \times 10^{-3}$  mm) two bands form simultaneously in regions A and C as shown in Spectrum III - 2. The band in region A is broad initially and the center of this band tends to shift toward higher frequency as coverage increases. At the same time the band in region C grows at a constant frequency of  $2035 \text{ cm}^{-1}$ . As the equilibrium pressure is increased above  $1 \times 10^{-3}$  mm, a band in region B begins to form and the center of this band tends to shift slightly to higher frequency as coverage increases. Simultaneously an increase

Figure II 10% Ni

Typical CO Adsorption Isotherms at Room Temperature

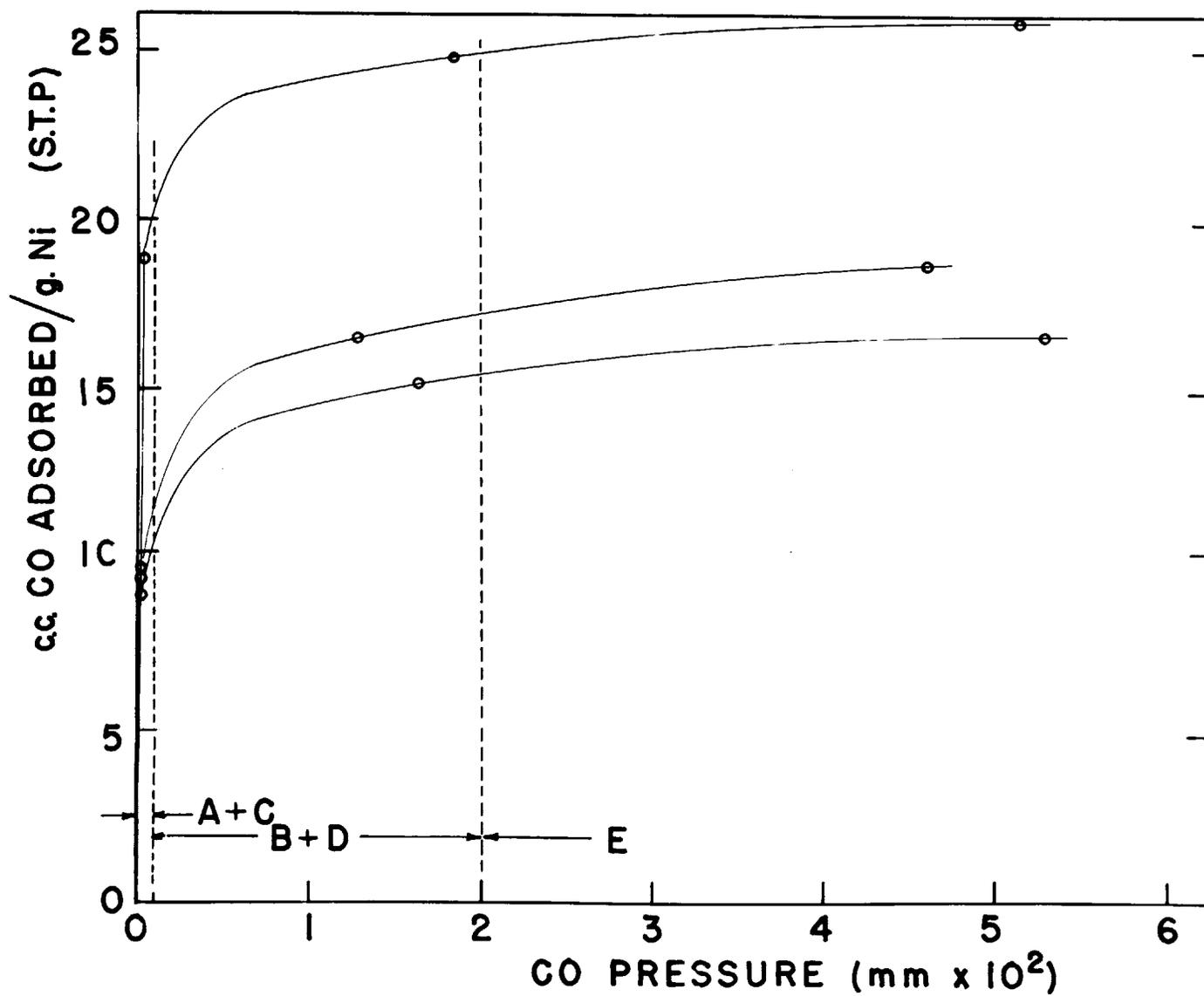
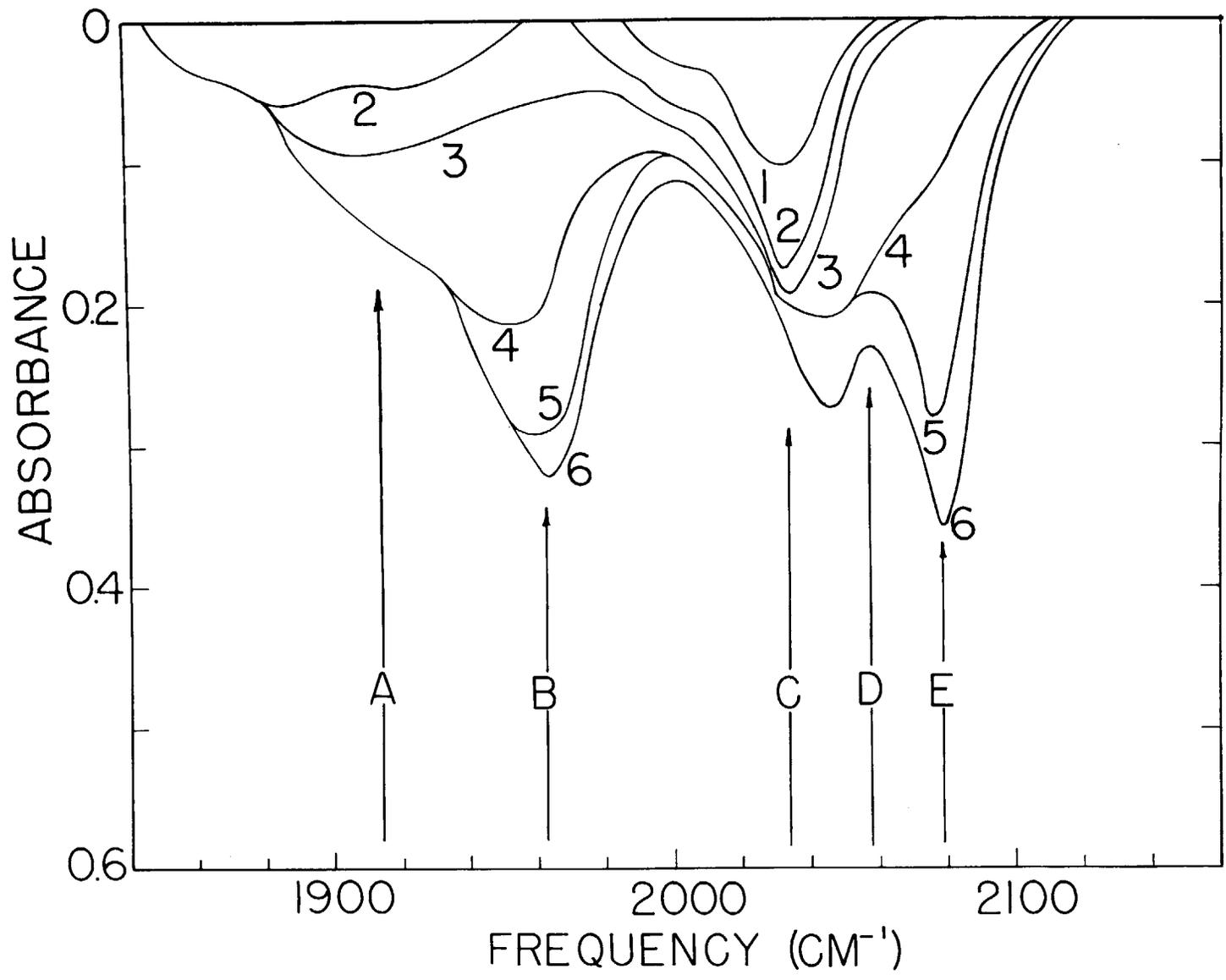


Figure III 10% Ni

Sample No. C-295

Sample Weight 0.134 g

<u>Spectrum</u>	<u>CO Pressure</u>	<u>Treatment</u>
1	$1.7 \times 10^{-4}$ mm	Stepwise addition of CO
2	$2.0 \times 10^{-4}$ mm	" " " "
3	$3.5 \times 10^{-4}$ mm	" " " "
4	$2.3 \times 10^{-2}$ mm	" " " "
5	1.2 mm	" " " "
6	1.2 mm	After 12 hours



in absorbance is observed on the high frequency side of the band at  $2035 \text{ cm}^{-1}$  and this is designated as lying in region D (Spectrum III - 4). As the pressure is raised above  $2 \times 10^{-2}$  mm a sharp band begins to form at  $2078 \text{ cm}^{-1}$  (designated E) and simultaneously the band in region B grows as the pressure is raised (Spectrum III - 5). On allowing the sample to sit 12 hr. at 1 mm CO pressure, slight intensification of the bands in regions B, C, D, and E occurs (Spectrum III - 6).

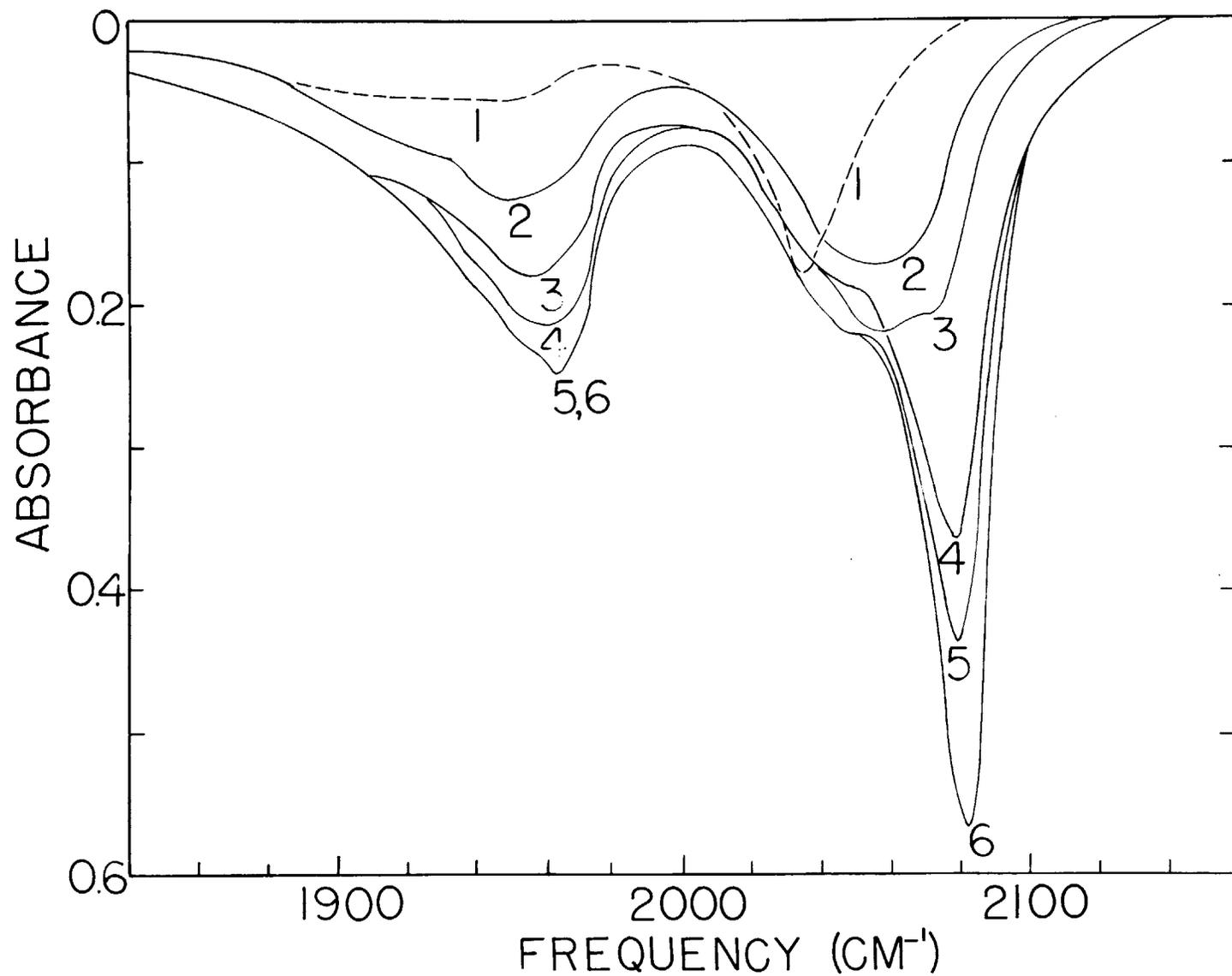
Figure IV shows the stepwise growth of bands for another 10% Ni sample. There is qualitative agreement between the stepwise growth of the various bands in this sample and the sample of Figure III. Spectrum IV - 5 corresponds to an equilibrium condition achieved after standing 12  $\frac{3}{4}$  hours, at a CO pressure of 0.7 mm, and is in agreement with the final spectrum (III - 6) obtained on the previous sample. On raising the CO pressure above several mm it is observed that a very intense band at  $2058 \text{ cm}^{-1}$  forms. This intense band corresponds to the formation of  $\text{Ni}(\text{CO})_4$  gas within the cell<sup>20</sup> as shown by the fact that it may be completely removed by pumping in 20 - 30 seconds. It has also been shown on another sample that the  $\text{Ni}(\text{CO})_4$  is primarily in the gas phase by using a semicircular sample plate. By rotating the sample cell about its vertical axis the beam was passed either through the sample or through the gas phase alone. Equivalent absorbances at  $2058 \text{ cm}^{-1}$  were obtained through the sample plus gas phase and through the gas phase alone. Spectrum IV - 6 shows the bands due to surface species after equilibration at 14.5mm

Figure IV 10% Ni

Sample No. C-264

Sample Weight 0.059 g

<u>Spectrum</u>	<u>CO</u>	<u>Pressure</u>	<u>Treatment</u>
1		$3 \times 10^{-4}$ mm	Stepwise addition of CO
2		$6.5 \times 10^{-3}$ mm	" " " "
3		$2.8 \times 10^{-2}$ mm	" " " "
4		0.7 mm	" " " "
5		0.7 mm	After 12 3/4 hours
6		14.5 mm	After 4 hours Pumped 20 seconds



CO pressure for 4 hours. During this time  $\text{Ni}(\text{CO})_4$  gas formed by reaction was present within the cell. Spectrum IV - 6 was obtained after pumping for 20 seconds to remove the excess CO gas and the  $\text{Ni}(\text{CO})_4$  gas from the cell. From measurements of the rates of desorption of even the most weakly held surface species it is reasonable to assume that very little change occurs in the band intensities for the adsorbed species during a pump-off period of 1 minute or less.

It may be seen that this treatment with CO at a pressure higher than the several mm pressure necessary to form  $\text{Ni}(\text{CO})_4$  gas results in stronger absorption in region E compared to the sample which was equilibrated at 1 mm CO pressure.

B. Stepwise Addition of  $\text{Ni}(\text{CO})_4$  (gas) to 10% Ni Samples

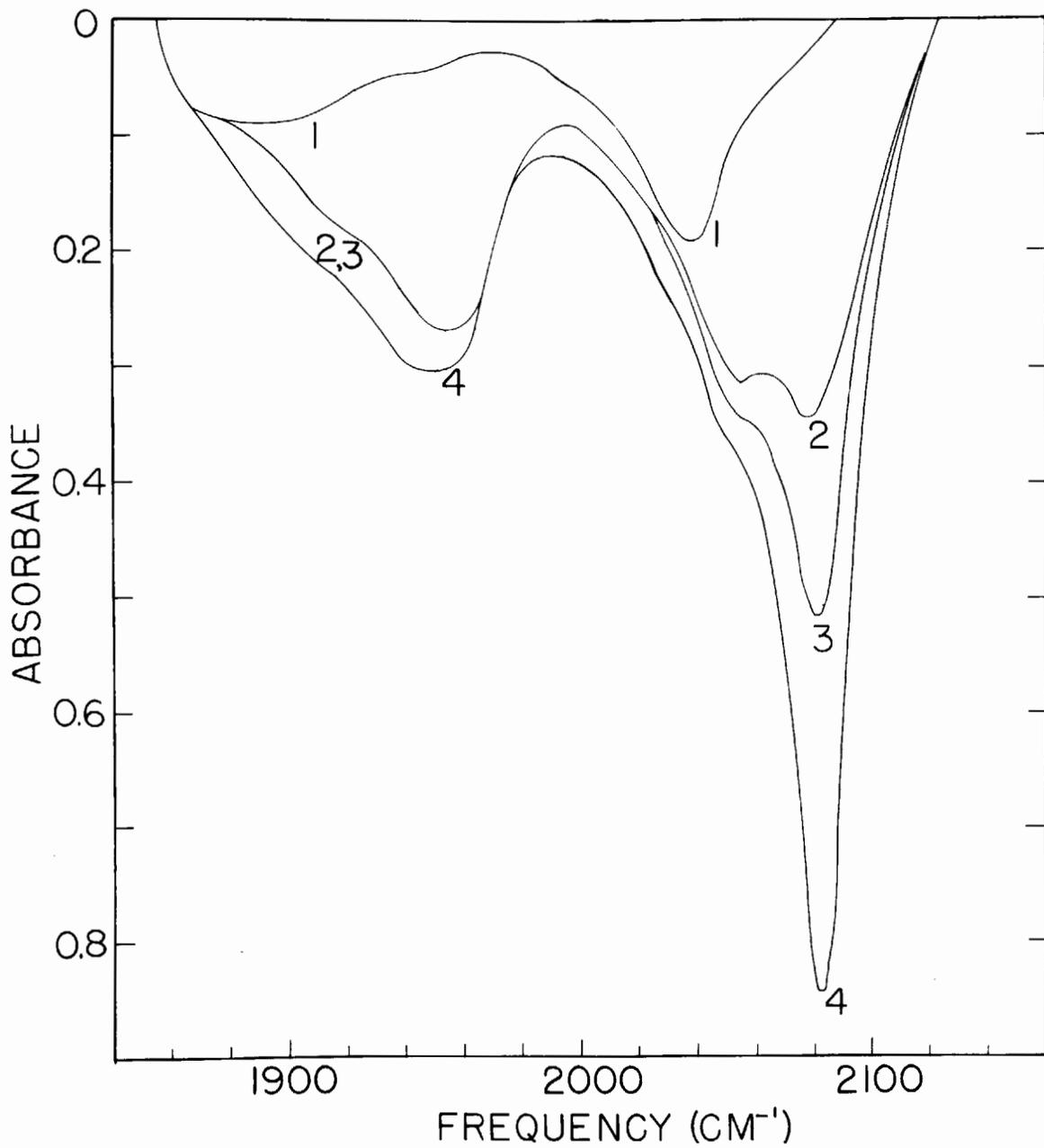
10% Ni samples, freshly reduced, were treated with  $\text{Ni}(\text{CO})_4$  gas in an attempt to observe differences which might exist in approaching the equilibrium situation from the  $\text{Ni}(\text{CO})_4$  side. Typical spectra are shown in Figure V. The first three stepwise spectra resemble those obtained when only CO was added to 10% Ni samples. Also, no undecomposed  $\text{Ni}(\text{CO})_4$  gas was observed in the cell until after spectrum V-3. Spectrum V-4 was recorded after allowing the sample to sit in the presence of an excess of  $\text{Ni}(\text{CO})_4$  gas at approximately 2.3 mm  $\text{Ni}(\text{CO})_4$  pressure overnight and then pumping for 30 seconds. If all the  $\text{Ni}(\text{CO})_4$  were decomposed, the maximum CO pressure would be 9.2 mm under these conditions, but the presence before pumping of the strong  $\text{Ni}(\text{CO})_4$  gas band at  $2058 \text{ cm}^{-1}$  indicates that complete decomposition of the  $\text{Ni}(\text{CO})_4$

Figure V 10% Ni

Sample No. C-474

Sample Weight 0.139 g

<u>Spectrum</u>	<u>CO Pressure</u>	<u>Treatment</u>
1	--	0.0174 cm <sup>3</sup> Ni(CO) <sub>4</sub> gas added at S.T.P.
2	--	0.087 cm <sup>3</sup> Ni(CO) <sub>4</sub> gas added at S.T.P.
3	--	0.146 cm <sup>3</sup> Ni(CO) <sub>4</sub> gas added at S.T.P.
4	--	2.1 cm <sup>3</sup> Ni(CO) <sub>4</sub> gas added at S.T.P.  After 12 hours, pumped 30 seconds



did not occur. Spectrum V - 4 displays an abnormally strong absorption in region E compared to the full coverage spectra in Figures III or IV.

C. Stepwise Addition of CO to a 1.5% Ni Sample

In order to obtain sufficient infrared absorption on samples containing 1.5% Ni it was necessary to use sample deposits heavier than those used for 10% samples. A typical isotherm for a 1.5% Ni sample is shown in Figure VI. Equilibrium pressures were obtained with a thermocouple gauge. The dead space correction, which would have been excessive if the McLeod gauge had been used, was minimized with the thermocouple gauge. At the highest pressure shown, the dead space correction amounts to about 30% of the total gas added to the sample cell. The accuracy obtainable with the thermocouple gauge in the pressure range shown is of the order of 10 - 20% so that the isotherm is of qualitative significance only.

Figure VII shows two spectra obtained on stepwise addition of CO to a typical 1.5% Ni sample. Spectrum VII - 1 corresponds to an equilibrium CO pressure of about 1.5 mm. At this stage it is evident that slight infrared absorption occurs in region A and stronger absorption in regions D and E. On adding CO to 11.5 mm,  $\text{Ni}(\text{CO})_4$  gas was observed to form within the cell. The  $\text{Ni}(\text{CO})_4$  gas and the excess CO were pumped away in 30 seconds and Spectrum VII - 2 shows the situation on the sample surface after this treatment. The band in region E has grown more intense. Infrared absorption in regions B and C is negligible even at the highest coverage.

Figure VI 1.5% Ni

Typical CO Adsorption Isotherm at Room Temperature

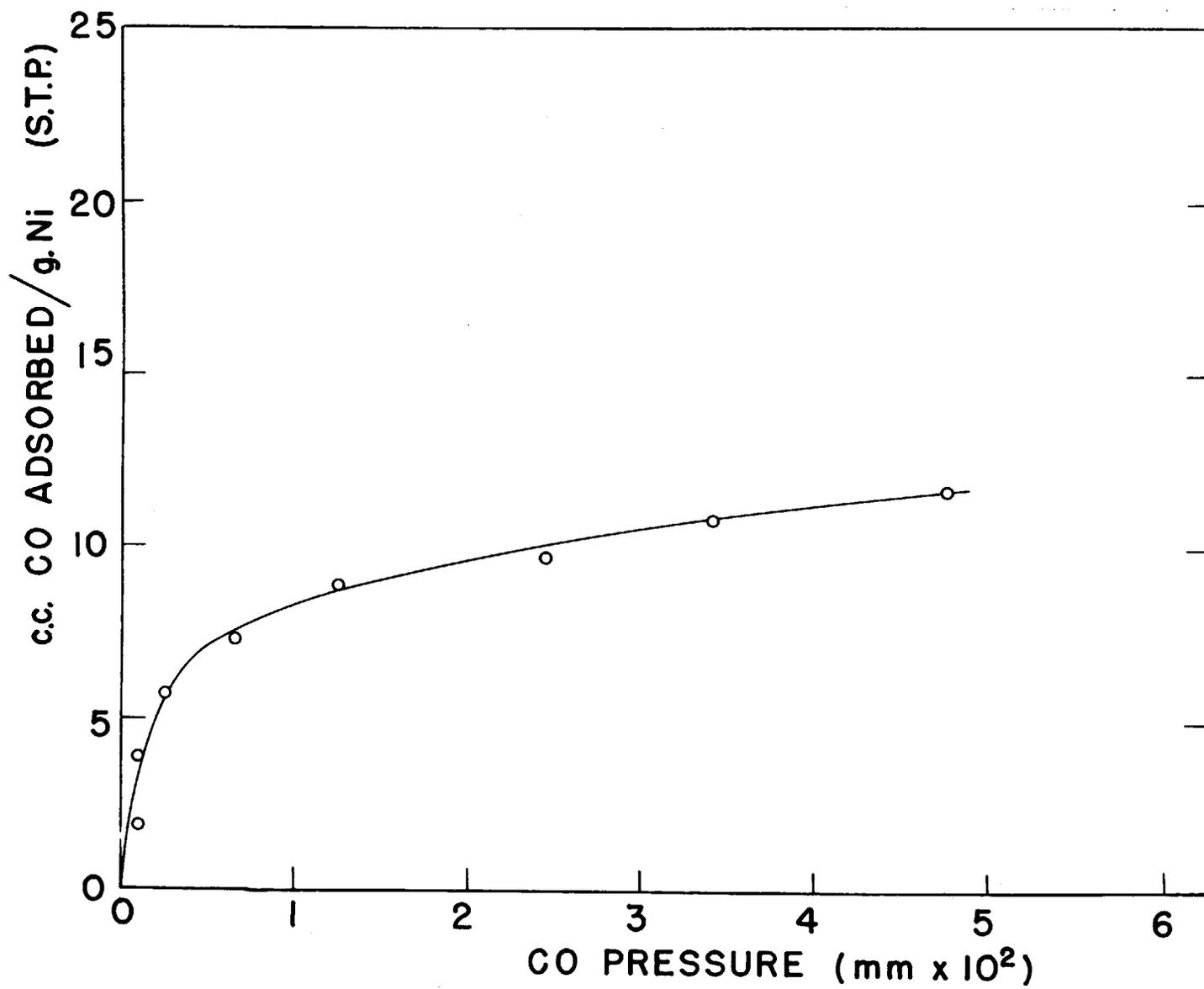
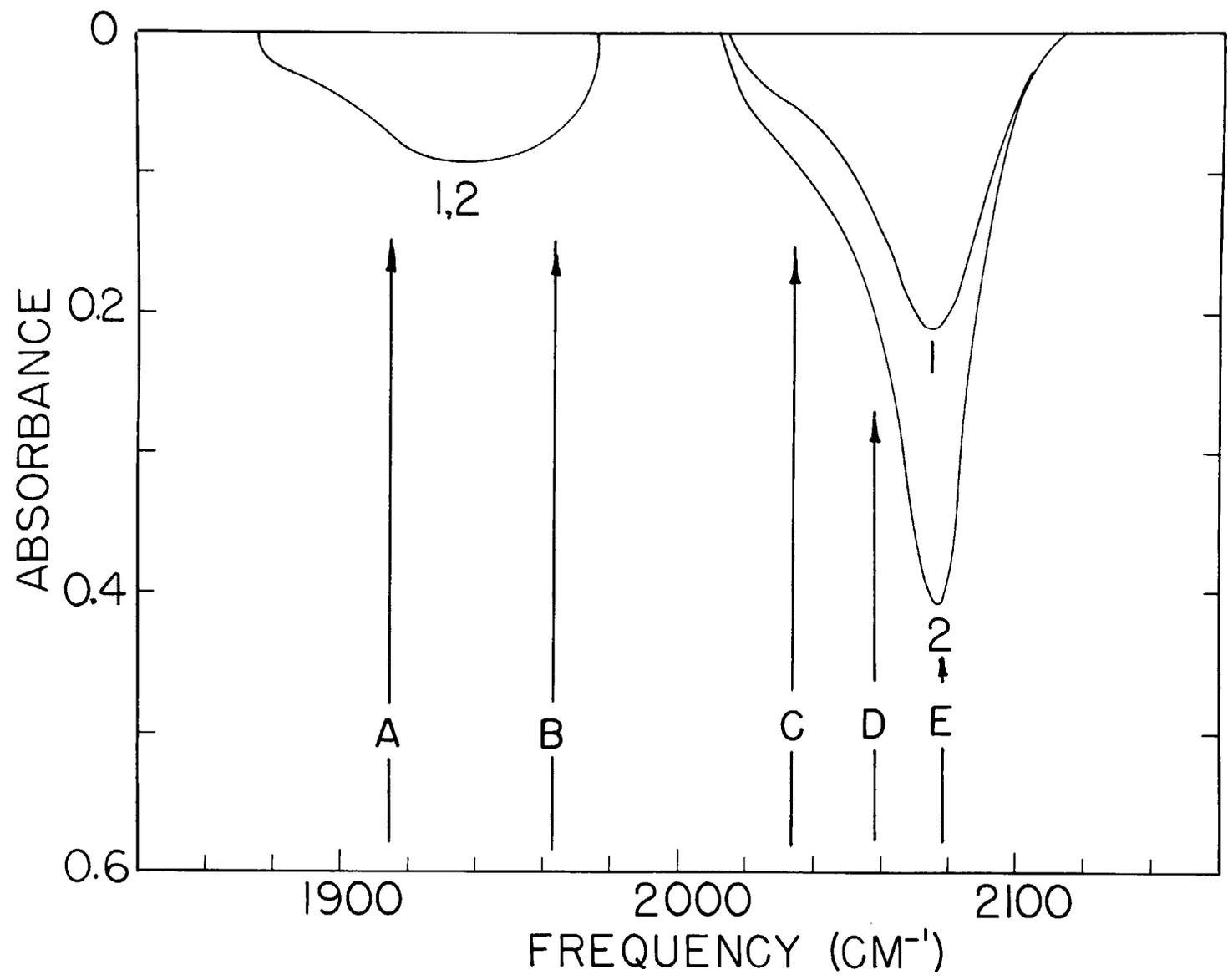


Figure VII 1.5% Ni

Sample No. C-360

Sample Weight 0.250

<u>Spectrum</u>	<u>CO Pressure</u>	<u>Treatment</u>
1	1.5 mm	Stepwise addition of CO
2	11.5 mm	Pumped 30 seconds



1000 2000

D. Stepwise Addition of Ni(CO)<sub>4</sub> (gas) to a 1.5% Ni Sample

Originally it was thought that the sharp band which was observed in region E on 10% Ni samples represented the presence of a molecular species which was the precursor to the formation of Ni(CO)<sub>4</sub> gas within the cell. This suspicion arose as a natural consequence of the fact that band E is the last band to form on stepwise adsorption of CO before Ni(CO)<sub>4</sub> gas begins to form and also that band E could be made abnormally intense by decomposing Ni(CO)<sub>4</sub> gas on fresh 10% Ni samples. It thus seemed likely that band E might represent a surface species containing more than one CO molecule per active Ni.\* Because of the fact that only a small fraction of the Ni within any given sample seems to be active under the conditions employed in this work, quantitative measurements of CO uptake per gram of Ni do not allow any estimate to be made of multiple adsorption.

The only reasonable approach to this problem which has been found involves decomposing measured quantities of Ni(CO)<sub>4</sub> gas on 1.5% Ni samples. By measuring the increase in CO pressure within the cell after each Ni(CO)<sub>4</sub> addition it was possible to calculate the ratio of the number of moles of CO gas liberated to the number of moles of Ni(CO)<sub>4</sub> gas decomposed. This ratio, called Z, is plotted versus the

\*This possibility has been suggested by Eischens and coworkers. See reference 7.

equilibrium CO pressure as shown in Figure VIII for three 1.5% Ni samples. The resulting stepwise spectra for one of the samples is shown in Figure IX, and the numbering of the solid points in Figure VIII corresponds to the numbered spectra. The Z versus pressure data were obtained with a thermocouple gauge. CO pressures were measured by multiple expansion in a system composed of known volumes. Since both the accuracy and precision of this gauge are poor, the curve presented in Figure VIII has only qualitative significance.

Measurements of Z and of the spectra were made up to the point where the presence of undecomposed  $\text{Ni}(\text{CO})_4$  gas was indicated by the spectra. It may be seen that the spectra resemble those obtained on stepwise adsorption of CO on a 1.5% Ni sample. Initially, when  $Z < 3$ , Spectra IX - 1 and IX - 2 show absorption in region D. As coverage was increased, the sharp band in region E developed and Z became approximately 3. At an equilibrium CO pressure greater than about 1 mm, undecomposed  $\text{Ni}(\text{CO})_4$  gas was present within the cell, and measurements of Z were discontinued.

Spectrum IX - 7 shows a broad band in region A. Spectra were not recorded in this region before this particular spectrum so we do not have a stepwise picture of developments in this region. In all probability the band in region A formed during the early stages of the  $\text{Ni}(\text{CO})_4$  addition. This would agree with the stage of appearance of a similar band observed when CO is adsorbed on a 10% Ni sample (Spectrum III - 2).

Figure VIII 1.5% Ni

Stepwise Addition of  $\text{Ni}(\text{CO})_4$  gas (Quantitative)

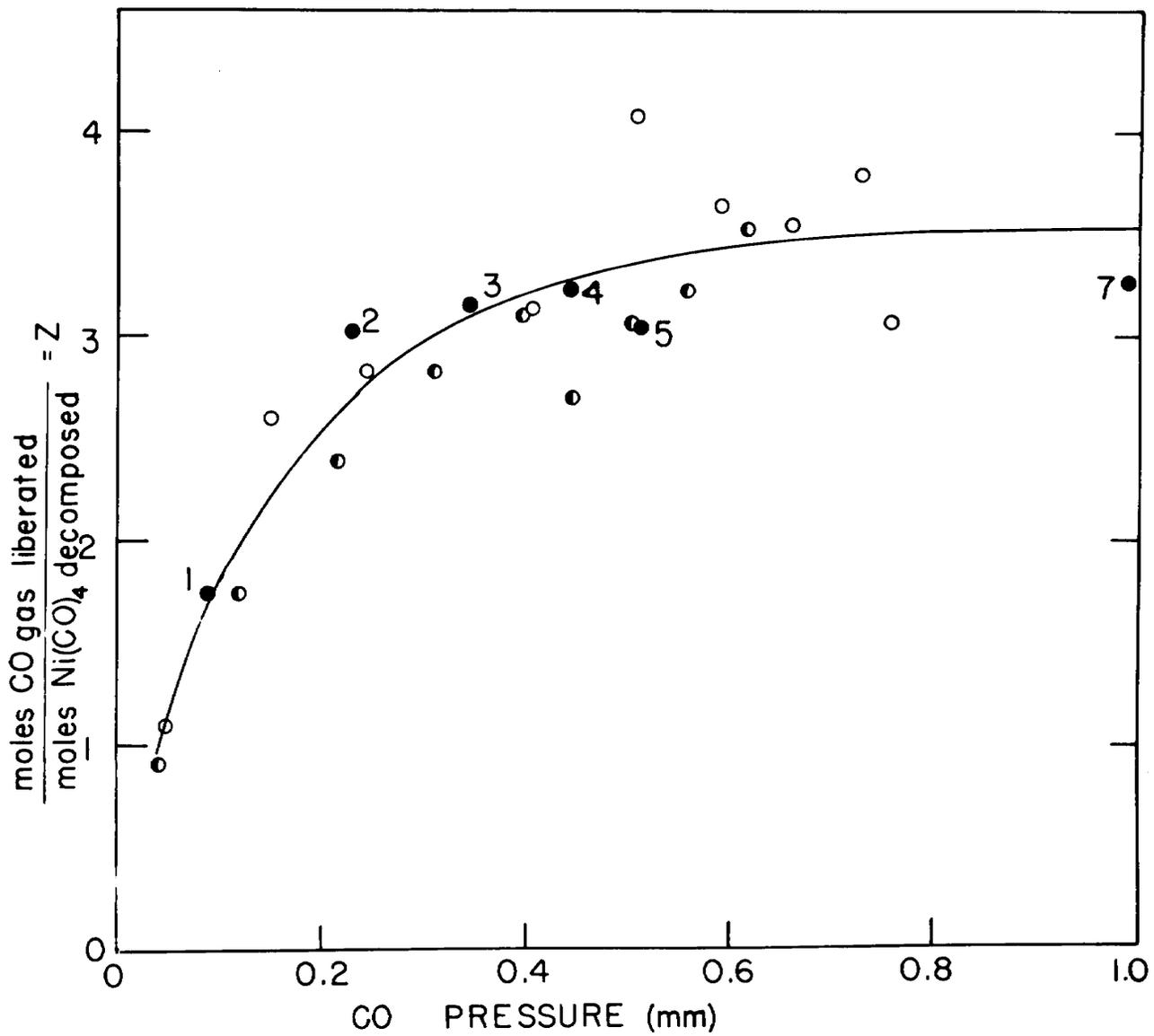


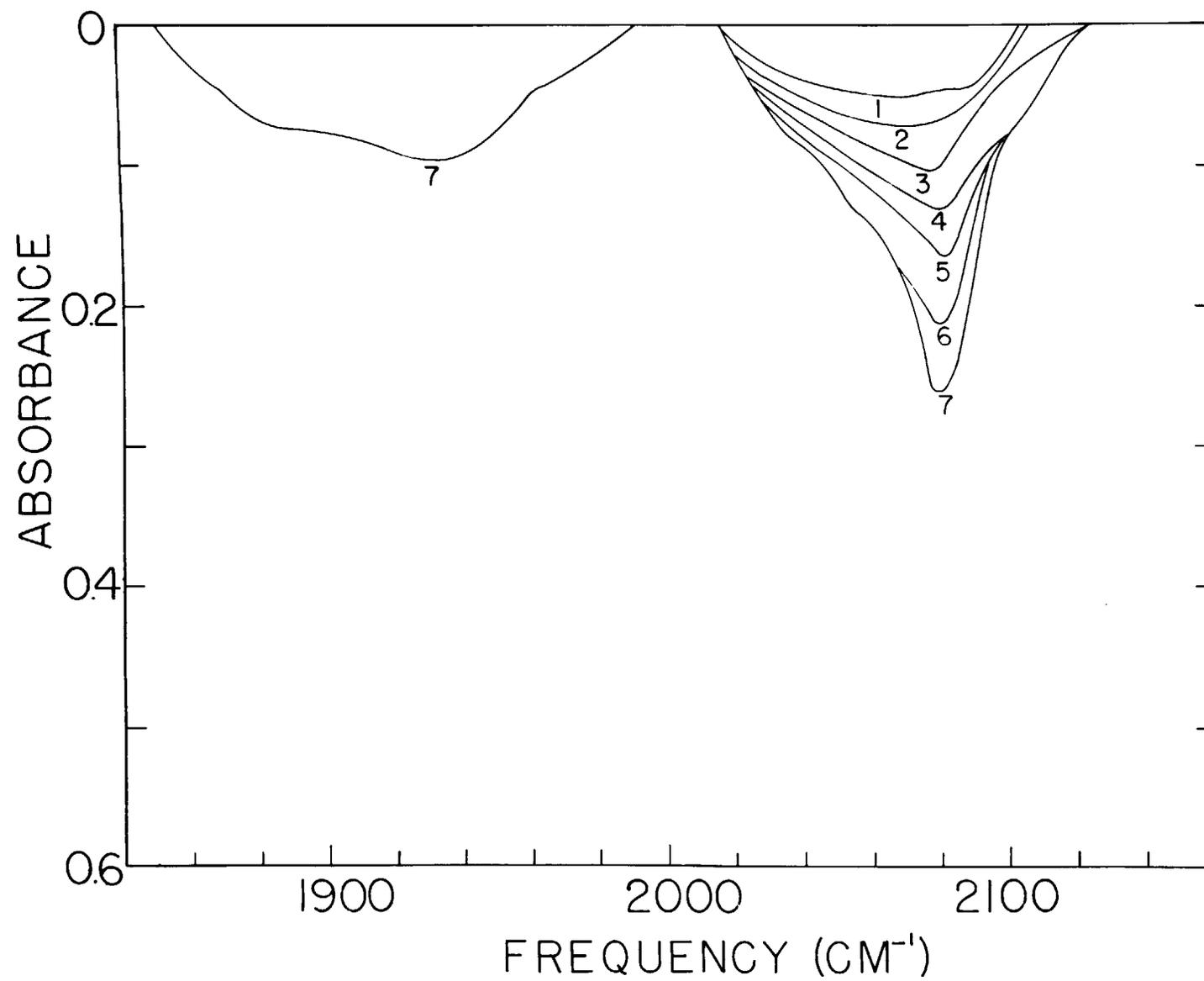
Figure IX 1.5% Ni

Stepwise Addition of  $\text{Ni}(\text{CO})_4$  gas (Quantitative)

Sample No. C-488

Sample Weight 0.263 g

<u>Spectrum</u>	<u>CO Pressure</u>	<u>Treatment</u>
1	0.088 mm	Stepwise addition of $\text{Ni}(\text{CO})_4$
2	0.266 mm	"
3	0.343 mm	"
4	0.441 mm	"
5	0.510 mm	"
6	0.837 mm	"
7	0.990 mm	"



#### E. Stepwise Adsorption of CO on a 25% Ni Sample

Since the relative intensities of the various infrared bands differ between 10% and 1.5% samples, an experiment was performed in which stepwise addition of CO was carried out on a 25% Ni sample as shown in Figure X. Because of the high Ni concentration, the total weight of Ni in the sample is about twice that used for 10% samples. The total uptake of CO was about 3 times that observed for normal 10% samples, corresponding at least in part to the higher total weight of Ni in this sample. Spectra X - 1 and X - 2 show absorbance initially in regions A and C, corresponding to the initial stages observed on 10% samples. At higher coverage (X - 3) strong growth is observed in regions A, B, and C, and the full coverage spectrum (X - 4) shows only slight development of absorption in regions D and E. This last spectrum was recorded after pumping 30 seconds on the sample which previously sat for about 6 hours with approximately 5 mm CO pressure and with some  $\text{Ni}(\text{CO})_4$  formed by reaction at this CO pressure. The relative intensity of band E in this 25% sample is low in relation to bands A, B, and C when compared to the relative intensity observed on 10% Ni samples at full coverage.

#### F. Stripping of a 10% Ni Sample with CO

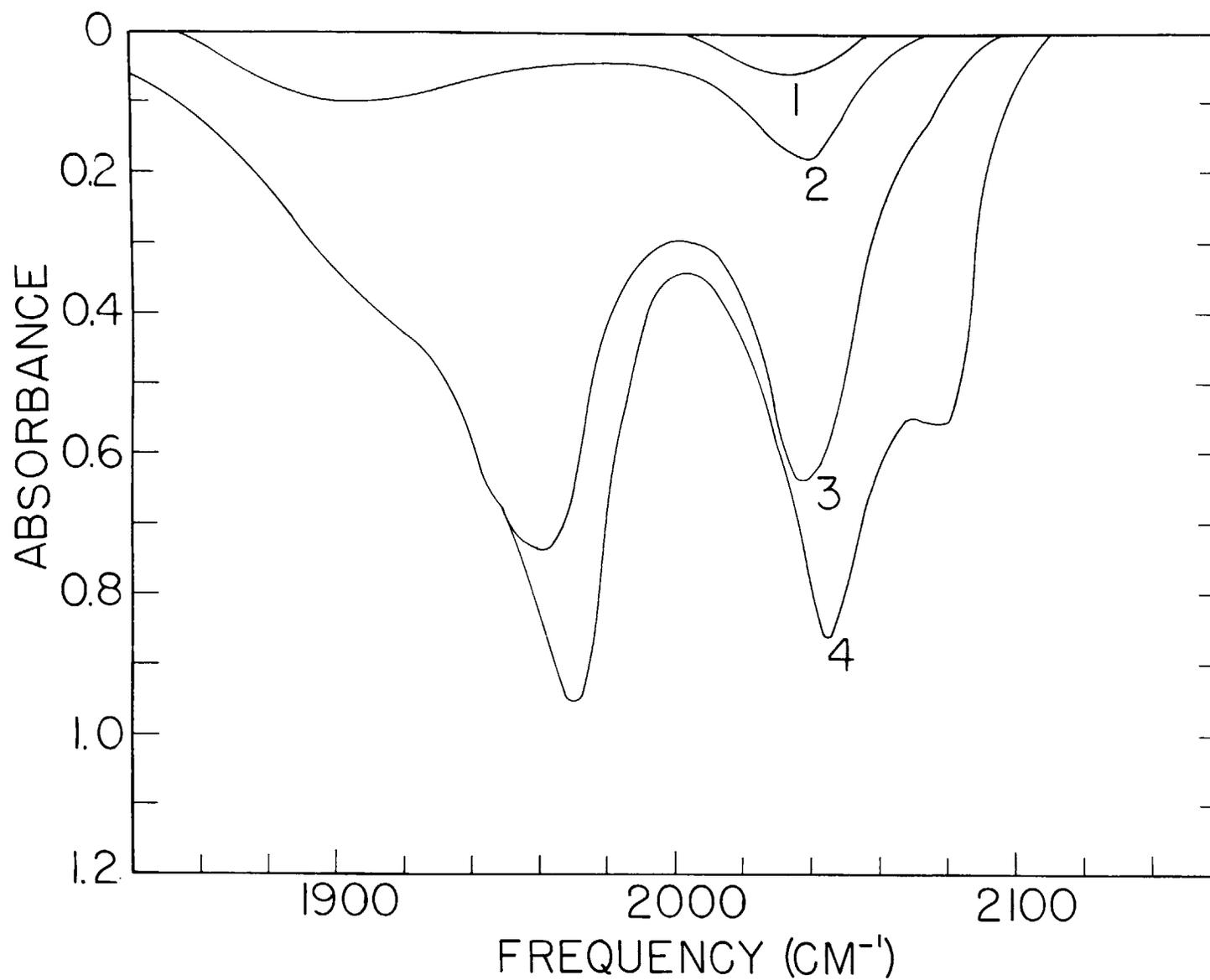
The fact that  $\text{Ni}(\text{CO})_4$  gas is observed to form with samples treated with CO at about 5 mm pressure afforded a convenient method of varying the concentration of Ni within a given sample as a function of time while maintaining full

Figure X 25% Ni

Sample No. C-541

Sample Weight 0.080 g

<u>Spectrum</u>	<u>CO Pressure</u>	<u>Treatment</u>
1	$4 \times 10^{-4}$ mm	Stepwise Addition of CO
2	$5 \times 10^{-4}$ mm	" " " "
3	$2.4 \times 10^{-3}$ mm	" " " "
4	5.3 mm	Sat 6 hours Pumped 30 seconds



coverage of CO. The  $\text{Ni}(\text{CO})_4$  gas produced was sublimed into a cold trap at  $77^\circ\text{K}$  as rapidly as it was formed thereby causing a continual removal of Ni from the sample. Spectra were recorded at intermediate stages of this treatment as shown in Figure XI; spectrum XI-1 shows the normal full coverage situation for a 10% Ni sample at an equilibrium CO pressure of 1 mm. No  $\text{Ni}(\text{CO})_4$  gas is present in the cell at this pressure. Spectrum XI-2 taken after 30 seconds pumping shows the situation after 3 days treatment at a CO pressure of about 59 mm. Spectrum XI-3 shows the surface band remaining after an additional 2.5 days treatment with CO at about 117 mm. This spectrum was taken after 10 minutes of pumping and may not accurately represent the situation with regard to surface bands at this final stage due to some desorption.

White crystals of  $\text{Ni}(\text{CO})_4$  were observed to form within the cold trap during this treatment. Also, the color of the sample changed from black to brown to tan as the Ni stripping operation was carried out. The transmittance of white light as judged by eye through the sample increased also as treatment with CO was continued.

#### G. Desorption of CO from a Full-coverage 25% Ni Sample

CO was desorbed from the full-coverage 25% Ni sample of Figure X by pumping the cell at  $10^{-5}$  -  $10^{-6}$  mm at room temperature. The infrared absorption bands disappeared in essentially the reverse order of appearance on the initial stepwise adsorption. The band of region E disappeared completely in approximately 30 minutes desorption. Simultaneous-

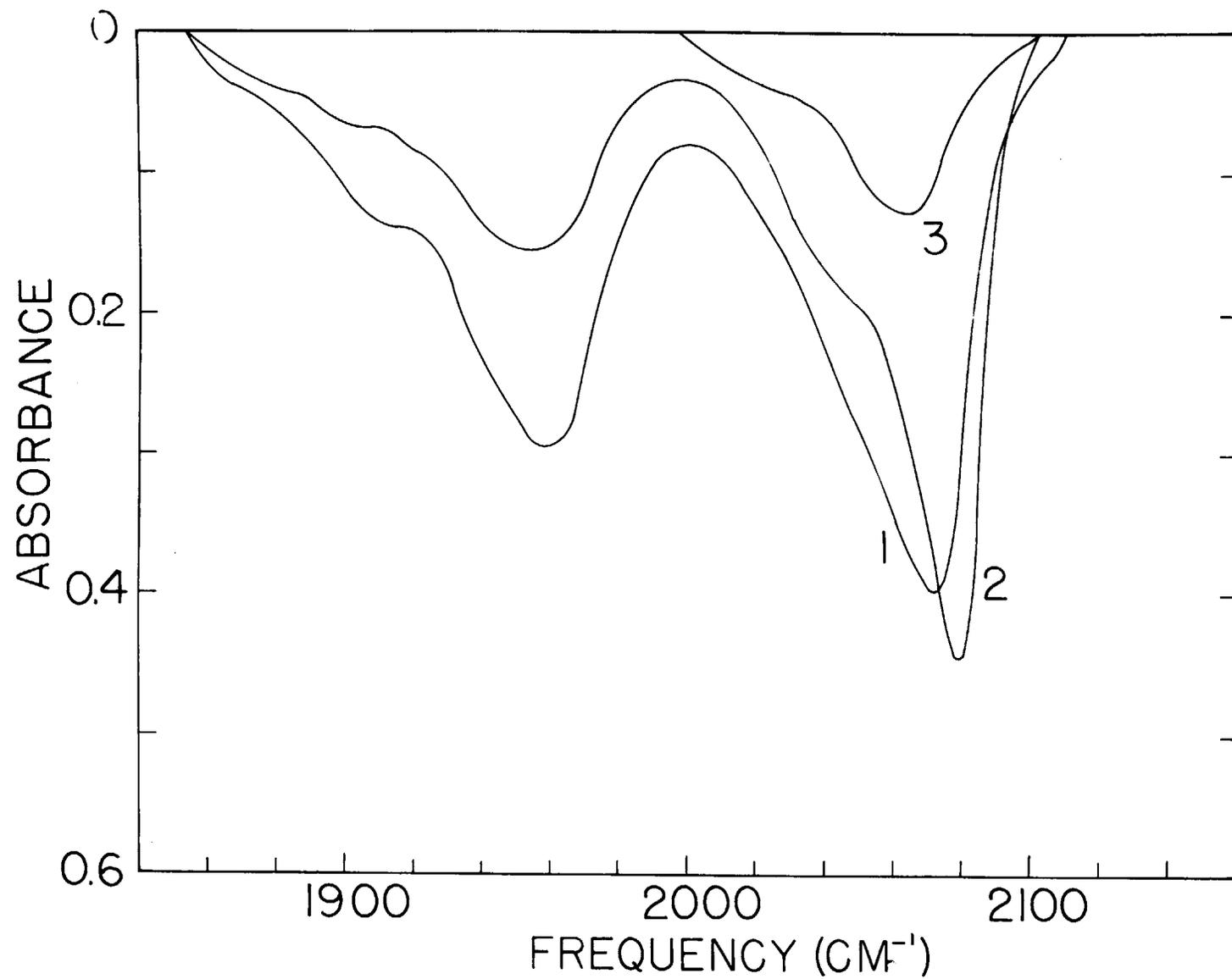
Figure XI 10% Ni

Stripping the Ni Surface with CO

Sample No. C-419

Sample Weight 0.071 g

<u>Spectrum</u>	<u>CO Pressure</u>	<u>Treatment</u>
1	1 mm	
2	59 mm	After 3 days
3	117 mm	After additional 2.5 days



-ly a small loss of absorbance occurred on the high frequency side of the band in region B. After this initial 30 minute period, the changes observed occurred very slowly. Thus, in 40 hours desorption the band in region D has disappeared by continued loss of intensity from its high frequency side and one-half of the absorbance in region B has been removed. Desorption was continued for 200 hours, during which time the absorbance in region B disappeared and a small loss of intensity in region C occurred. Thus, after 200 hours desorption, a band in region A and a band in region C remain.

CO was readsorbed on the sample by adding sufficient CO gas to bring the CO pressure up to that pressure at which full coverage was originally achieved. This readsorption caused the spectrum to return to its original full-coverage intensity of absorbance in all regions. Thus extensive desorption at room temperature does not seem to alter the character of the Ni surface.

#### H. X-Ray Studies of the Ni Samples

In order to determine the extent of crystallinity existing in the Ni samples used in this work, X-ray powder photographs were made of a 25% Ni sample, a 10% Ni sample, and the Alon C support alone. Only the 25% sample gave any evidence of containing crystalline Ni particles; this sample gave broad lines corresponding to the three most intense lines observed for bulk Ni samples ( $d = 2.034 \text{ \AA}$ ;  $1.762 \text{ \AA}$ ;  $1.246 \text{ \AA}$ ). From an examination of the line widths obtained with the 25% Ni sample it was possible to estimate the average Ni

crystallite size,  $\bar{L}$ , on the 25% Ni sample as follows:<sup>32,33</sup>

$$\bar{L} = 0.89 \lambda / B_m \times \frac{2\pi}{360} \cos \theta$$

For the X-ray line corresponding to a d spacing of 1.762 Å: (Cu - K $\alpha$  radiation;  $\lambda = 1.540$  Å)

$$2\theta = 51.8^\circ \pm 1.15^\circ$$

$$B_m = 2(1.15^\circ) = 2.3^\circ = \text{estimated line width}$$

$$\bar{L} = 38 \text{ \AA}$$

$B_m$  has not been corrected for the small positive error due to finite sample size.

## I. Initial Investigations on the Effect of the Mercury Poisoning of Ni Surfaces

### 1. Stepwise desorption of a 10% Ni sample after full CO coverage: Hg poisoning.

A very interesting phenomenon was observed as a result of some room temperature desorption studies first made on 10% Ni samples on which CO had been adsorbed to full coverage. Figure XII shows a series of stepwise spectra recorded at various times during desorption. Spectrum XII-1, achieved at a CO pressure of 14.5 mm, shows the full coverage situation before desorption was begun. This is the same spectrum as Spectrum IV-6 and is presented again for convenience. Spectrum XII-2 was obtained after 5 minutes desorption using the diffusion pump which maintained the pressure below  $10^{-5}$  mm during desorption. The sharp band in region E has lost a

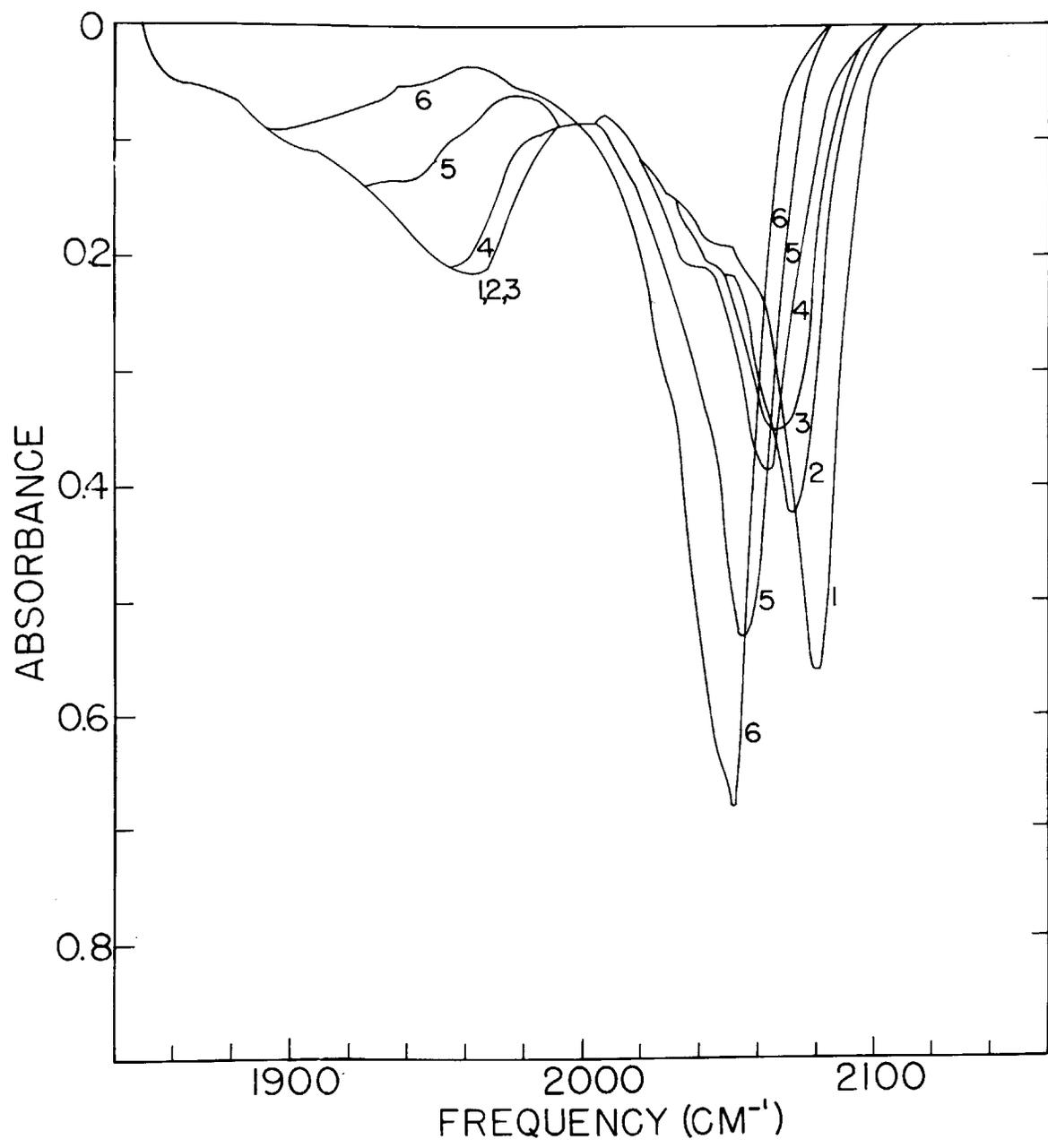
Figure XII      10% Ni

Stepwise Desorption; Hg Poisoning

Sample No. C-264

Sample Weight    0.059 g

<u>Spectrum</u>	<u>CO Pressure</u>	<u>Treatment</u>
1	14.5 mm	Sat 4 hours; pumped 20 sec.
2	--	Pumped 5 min.
3	--	Pumped 10 min.
4	--	Pumped 50 min.
5	--	Pumped 5 hours
6	--	Pumped 15 hours



great deal of its intensity and has begun to shift to lower frequency. The sharp band in region E (after a total of 10 minutes desorption) continues to exhibit this trend of shifting as shown in Spectrum XII-3. Spectrum XII-4 shows the situation after a total of 50 minutes desorption. Here a sharp reversal of trend is apparent. The peak intensity of the sharp band (now with absorbance maximum at  $2064\text{ cm}^{-1}$ ) has begun to increase. Also, a slight decrease in intensity on the high frequency side of the band in region B is evident. Spectra XII-5 and XII-6 portray the situation after 5 hours and 15 hours desorption respectively. Here the sharp band now in region D grows in a striking fashion while shifting to a final low frequency of  $2052\text{ cm}^{-1}$ . Simultaneously the band in region B disappears by continued loss of intensity on its high frequency side.

It will be shown that this striking effect of growth in region D is due to the accidental exposure of the sample to Hg vapor during the long desorption times employed. This Hg vapor originated from the McLeod gauge which was inadvertently allowed to remain open to the vacuum manifold during the desorption shown here.

2. Readsorption of CO on the Hg poisoned and partly desorbed 10% Ni sample.

Figure XIII shows the results of an investigation undertaken to determine the effect of adding CO to the poisoned and partly desorbed sample of Figure XII. Spectrum XIII-1 was obtained after a total of 24 hours desorption of

the 10% Ni sample of Figure XII. This spectrum is very similar to Spectrum XII-6 (obtained after 15 hours desorption) showing that after a certain point has been reached in the desorption-poisoning process, changes in the spectra occur much more slowly than before. Spectrum XIII-2 was obtained after adding 0.044 cc of CO (S.T.P.) to the sample. An increase in absorbance was produced and the frequency of the band increased from  $2052 \text{ cm}^{-1}$  to  $2059 \text{ cm}^{-1}$ . Figure XIII-3 resulted when CO was added to a pressure of about 0.79 mm. Here the band has shifted to  $2067 \text{ cm}^{-1}$ . Only a very slight increase in absorbance occurred in region B during this treatment and this region is not shown in Figure XIII.

It has been shown on several 10% samples that the process of shifting the sharp band back and forth between the limits  $2050 \text{ cm}^{-1}$  -  $2070 \text{ cm}^{-1}$  may be repeated many times by alternate adsorption and desorption of CO.

3. Stepwise desorption of a 1.5% Ni sample after full CO coverage: Hg Poisoning.

The formation of the intense band due to desorption plus Hg poisoning on 10% Ni samples could possibly be interpreted as a Hg induced rearrangement of a particular surface species initially present on the sample to give a new species corresponding to the intense band. Because the spectrum of CO adsorbed on 1.5% Ni samples is simpler than on 10% samples, the desorption - poisoning operation was carried out on a 1.5% Ni sample as shown in Figure XIV. Spectrum XIV-1 shows the full coverage situation in the C-

Figure XIII 10% Ni

Readsorption of CO on the Hg Poisoned and Partly  
Desorbed Sample

Sample No. C-264

Sample Weight 0.059 g

<u>Spectrum</u>	<u>CO Pressure</u>	<u>Treatment</u>
1	--	Pumped 24 hours
2	--	0.044 cm <sup>3</sup> CO added S.T.P.
3	0.79 mm	After 12 hours

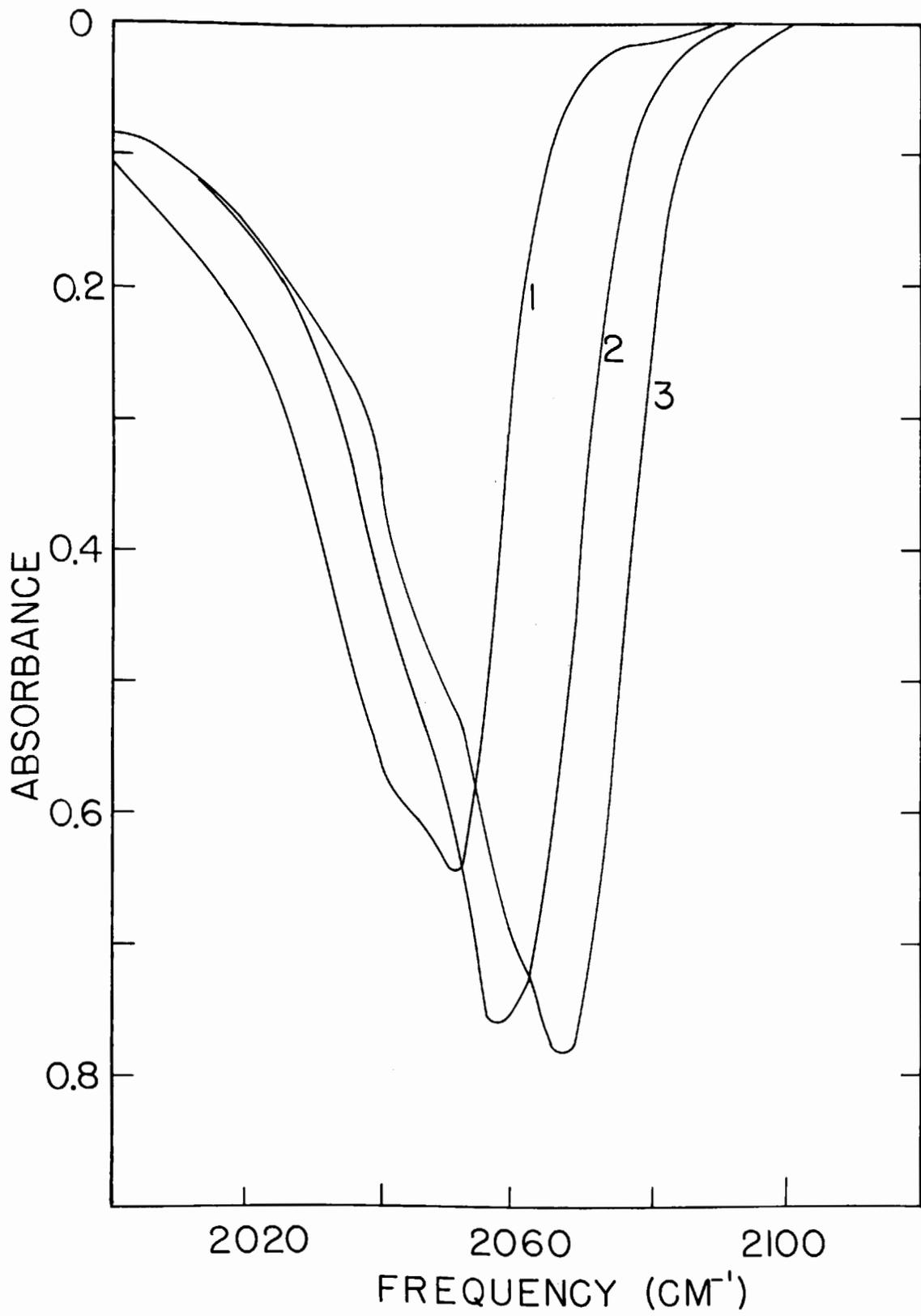


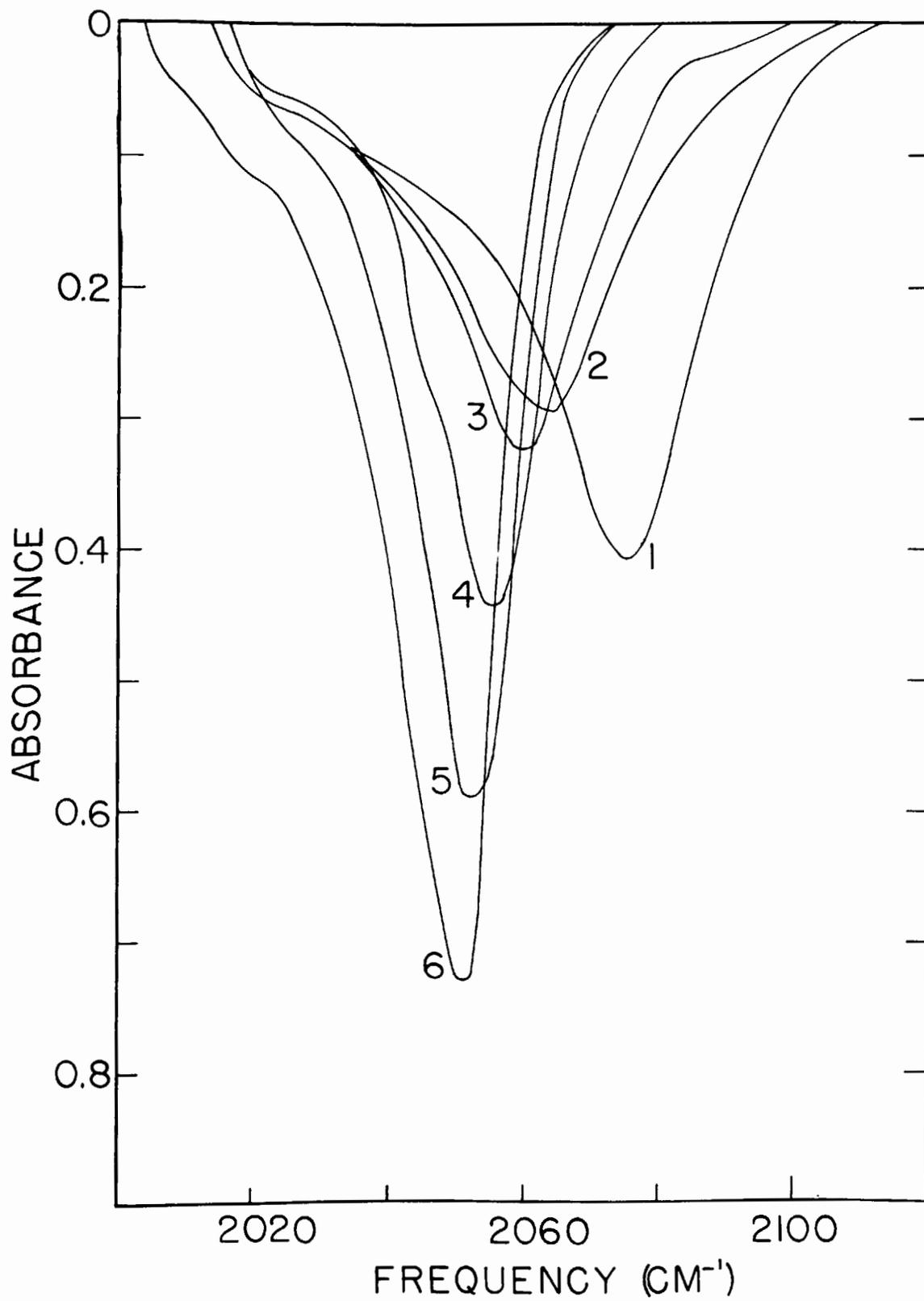
Figure XIV 1.5% Ni

Stepwise Desorption; Hg Poisoning

Sample No. C-360

Sample Weight 0.250 g

<u>Spectrum</u>	<u>CO Pressure</u>	<u>Treatment</u>
1	11.5 mm	Pumped 30 seconds
2	--	Pumped 10 minutes
3	--	Pumped 40 minutes
4	--	Pumped 3 hours
5	--	Pumped 7 3/4 hours
6	--	Pumped 23 hours



D-E region. A broad weak band in region A is not shown. This full-coverage situation was achieved by treatment with CO at 11.5 mm pressure at which pressure  $\text{Ni}(\text{CO})_4$  gas was produced by reaction, and the spectrum was taken after 30 seconds pumping to remove the excess CO and  $\text{Ni}(\text{CO})_4$  gas. Desorption plus poisoning over a period of hours was carried out in the same fashion as described for the 10% Ni sample which was shown in Figure XII. The general result (growth of a new band in region D) was identical to that observed with the 10% Ni sample. The final spectrum (XIV-6) was obtained after 23 hours desorption plus poisoning, and the frequency of the absorbance maximum of the prominent band has shifted to  $2051 \text{ cm}^{-1}$ .

4. Hg poisoning of a 10% Ni sample at full CO coverage and subsequent desorption under Hg free conditions.

The previous experiments in which CO desorption and Hg poisoning were carried on simultaneously did not distinguish the effect of either of these processes alone with 10% Ni samples. For this reason a 10% Ni sample was poisoned with Hg at full CO coverage as shown in Figure XV. Spectrum XV-1, recorded after 30 seconds pumping, is the full-coverage Hg free situation achieved by adding  $\text{Ni}(\text{CO})_4$  gas to a 10% Ni sample, thereby giving abnormally intense absorbance in regions D and E. Spectrum XV-2 was obtained after exposing the sample to Hg vapor for 3 hours at a Hg pressure of about  $1 \times 10^{-2}$  mm.

Spectrum XV-3 resulted after an additional

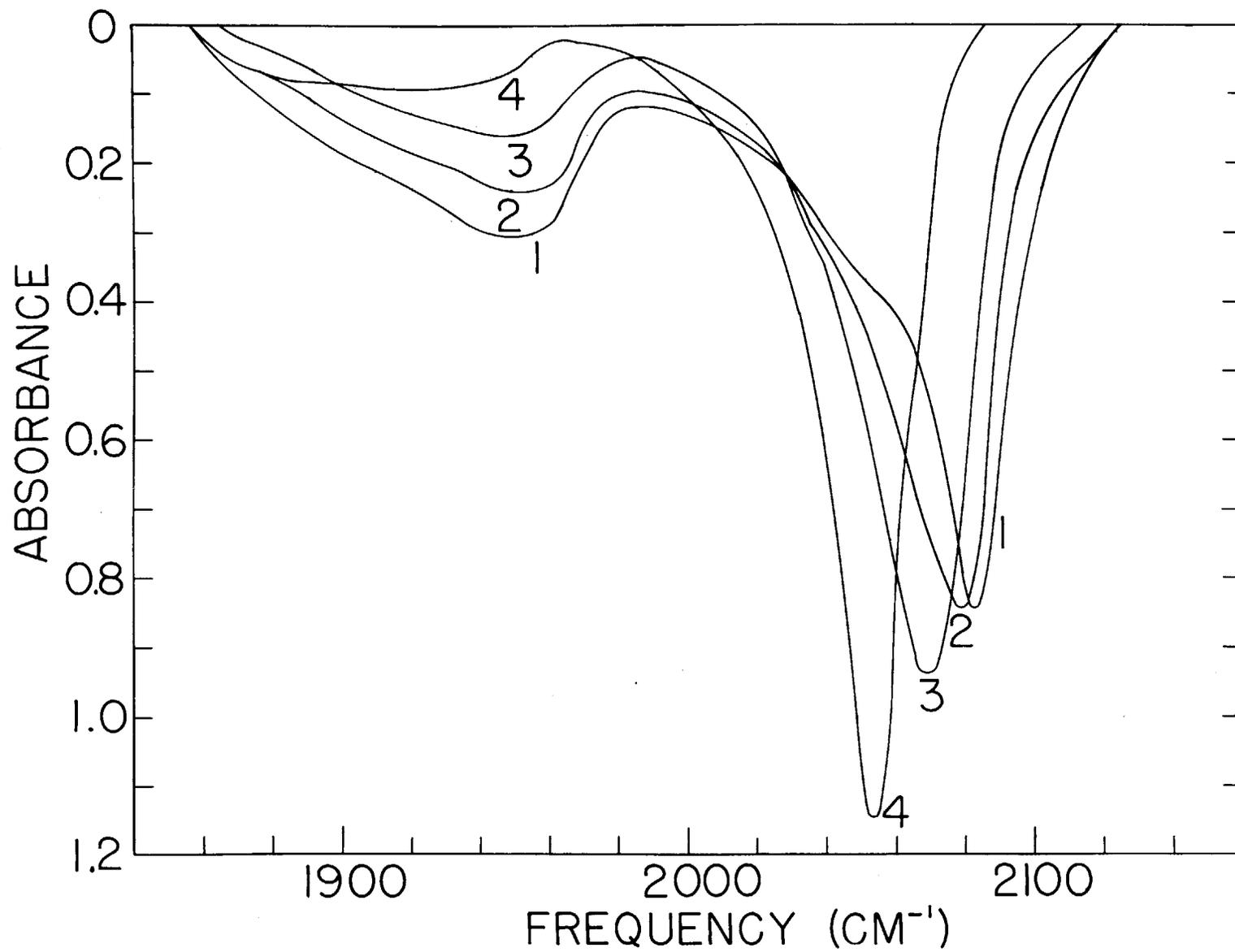
Figure XV 10% Ni

Hg Poisoning at Full CO Coverage

Sample No. C-474

Sample Weight 0.139 g

<u>Spectrum</u>	<u>CO Pressure</u>	<u>Treatment</u>
1	--	2.1 cm <sup>3</sup> Ni(CO) <sub>4</sub> gas added (S.T.P.); sat 12 hours; Pumped 30 sec.
2	--	Exposed to Hg vapor for 3 hours at $1 \times 10^{-2}$ mm.
3	--	Exposed to Hg vapor for 9.5 hours at 0.27 mm
4	--	Pumped 9.5 hours



treatment at a Hg vapor pressure of 0.27 mm for 9.5 hours. This extensive treatment with Hg resulted in the formation of an intense band in region D at  $2069\text{ cm}^{-1}$  and loss of intensity in region E. Simultaneously there was an overall intensity loss in regions A and B due to the Hg poisoning. The sample was then partially desorbed under Hg free conditions for 9.5 hours, and the situation which resulted from this desorption is shown by Spectrum XV-4. Here the sharp band formed in region D by the poisoning, increased in peak absorbance and shifted lower in frequency to  $2053\text{ cm}^{-1}$ . Also, a slight decrease in absorbance in the A-B region resulted from this desorption.

J. Addition of Mercury to a Partially Covered 1.5% Ni Sample

The rate of effect of Hg vapor on the spectrum of CO adsorbed on both 10% and 1.5% Ni samples during desorption indicated that the Hg poisoning under the conditions employed during desorption was a fairly slow process. Thus the striking change noted in the spectra due to the Hg poisoning was complete in a time of the order of 15 hours. Since desorption was occurring during all this time, it was plausible to suspect that the particular adsorbed CO molecules affected by Hg were rather strongly held, in contrast to the weakly held CO which is adsorbed at a relatively high pressure to form the band in region E.

To test the above hypothesis Hg was adsorbed on

a 1.5% Ni sample partially covered with CO as shown in Figure XVI. The Hg vapor pressure was maintained at about  $2 \times 10^{-3}$  mm during the poisoning.

Spectrum XVI-1 shows a fairly broad band centered at about  $2055 \text{ cm}^{-1}$  which resulted from the addition of CO to a pressure of  $4.75 \times 10^{-2}$  mm as measured on the thermocouple gauge. This equilibrium pressure corresponds roughly to completion of the band in region D. Very little development in region E has occurred at this stage of adsorption of CO.

Spectrum XVI-2 was obtained after 28 minutes exposure to the Hg vapor. A strong, sharp band has started to form, centered at  $2060 \text{ cm}^{-1}$ . The small absorbance originally present in region E has disappeared. Spectrum XVI-3 corresponds to a total of 47 minutes Hg poisoning. The sharp band continued to intensify at essentially constant frequency. Spectrum XVI-4 and XVI-5 were recorded after a total of 71 minutes and 112 minutes exposure to Hg respectively. The band has continued to intensify at a constant frequency of  $2060 \text{ cm}^{-1}$ . Spectrum XVI-6 was obtained after 14 hours exposure to the Hg vapor. The band has grown only slightly in this last 12 hour period of treatment and its frequency has shifted very slightly to  $2057 \text{ cm}^{-1}$ .

K. Desorption of the Sharp Band Formed by Mercury Poisoning on a 1.5% Ni Sample

Figure XVII represents a continuation of the spectra shown in Figure XVI. Spectrum XVII-1 is the same as

Figure XVI 1.5% Ni

Addition of Hg to Partly Covered Sample

Sample No. C-501

Sample Weight 0.291 g

<u>Spectrum</u>	<u>CO Pressure</u>	<u>Treatment</u>
1	$4.75 \times 10^{-2}$ mm	
2	--	Exposed to Hg vapor for 28 min. at $2 \times 10^{-3}$ mm
3	--	Exposed to Hg vapor for 47 min. at $2 \times 10^{-3}$ mm
4	--	Exposed to Hg vapor for 71 min. at $2 \times 10^{-3}$ mm
5	--	Exposed to Hg vapor for 112 min. at $2 \times 10^{-3}$ mm
6	--	Exposed to Hg vapor for 14 hours at $2 \times 10^{-3}$ mm

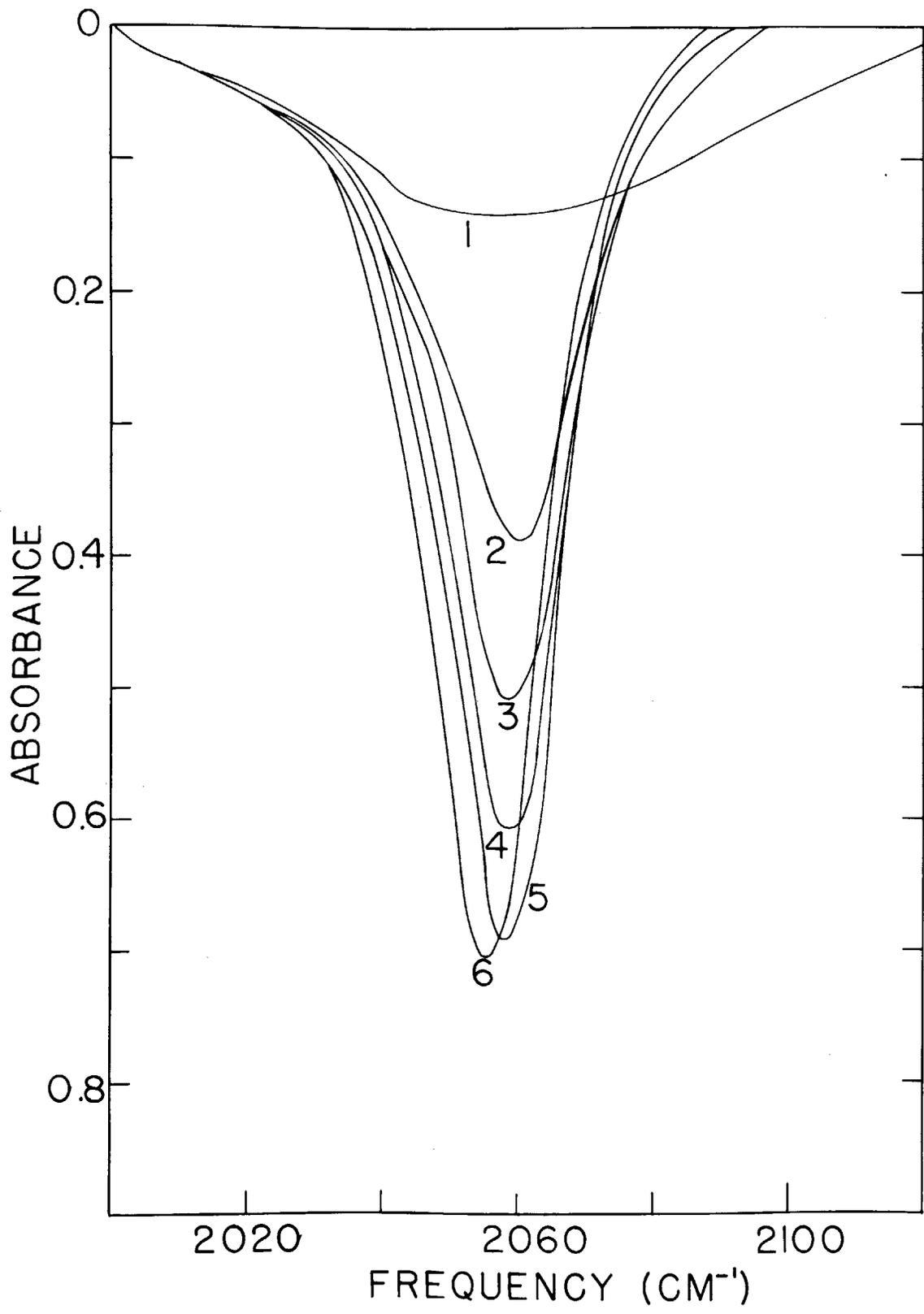


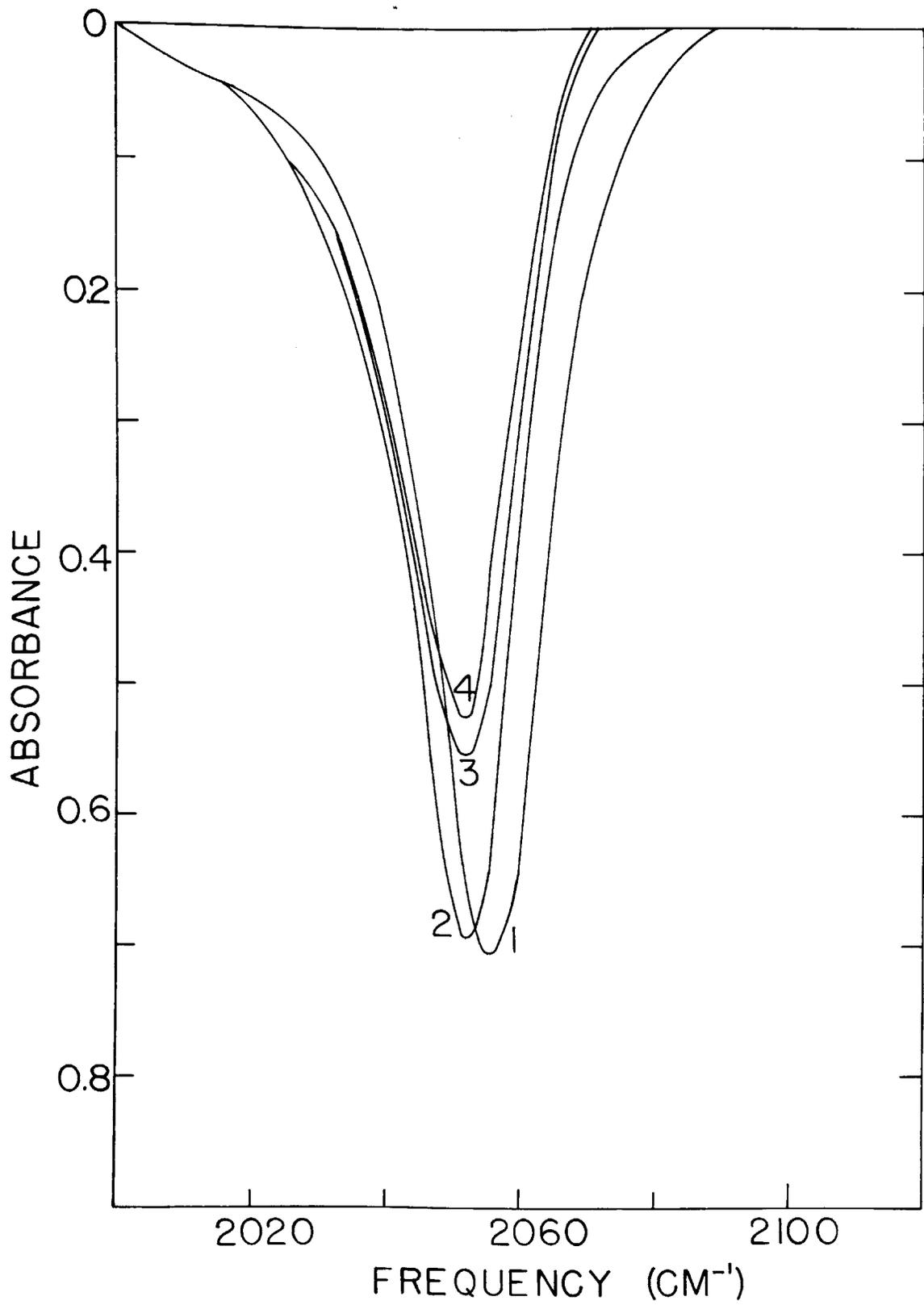
Figure XVII 1.5% Ni

Desorption of Hg Poisoned Sample

Sample No. C-501

Sample Weight 0.291 g

<u>Spectrum</u>	<u>CO Pressure</u>	<u>Treatment</u>
1	--	Exposed to Hg vapor for 14 hours at $2 \times 10^{-3}$ mm
2	--	Pumped 2 hours
3	--	Pumped 24 hours
4	--	Pumped 77 hours



XVI-6 (14 hours exposure to Hg) and is shown again for convenience. Spectrum XVII-2 was obtained after 2 hours desorption under Hg-free conditions. The sharp band has become slightly less intense and has shifted to  $2052 \text{ cm}^{-1}$ . Desorption was continued for 24 hours, giving Spectrum XVII-3; Spectrum XVII-4 was obtained after 77 hours desorption. The sharp band loses intensity very slowly at essentially constant frequency during desorption, and the rate of loss of intensity seems to be slower in the later states of desorption.

L. Desorption of CO from a 1.5% Ni Sample Which Has Been Partially Covered with CO and Partially Poisoned with Hg

Figures XVIII and XIX represent the formation and desorption of the first stages of the sharp band which results from the poisoning of a 1.5% Ni sample which is partially covered with CO. Spectrum XVIII-1 shows the fairly broad band in region D. Here the CO pressure is  $4.75 \times 10^{-2}$  mm. This band is essentially identical to the band shown in Spectrum XVI-1, in agreement with the fact that the CO pressures are the same. Spectrum XVIII-2 and XVIII-3 correspond to 14 minutes and 29 minutes treatment with Hg vapor, and Spectrum XVIII-3 agrees well with XVI-2 (28 minutes exposure) in intensity and position (both  $2060 \text{ cm}^{-1}$ ). At this point, when presumably the sample was only partially poisoned with Hg, desorption was begun under Hg-free conditions. Figure XIX shows the stepwise spectra obtained during desorption. Spectrum XIX-1 is the same as Spectrum XVIII-3,

Figure XVIII 1.5% Ni

Addition of Hg to Partly Covered Sample

Sample No. C-522

Sample Weight 0.279 g

<u>Spectrum</u>	<u>CO Pressure</u>	<u>Treatment</u>
1	$4.75 \times 10^{-2}$ mm	
2	--	Exposed to Hg vapor for 14 minutes at $2 \times 10^{-3}$ mm
3	--	Exposed to Hg vapor for 29 minutes at $2 \times 10^{-3}$ mm

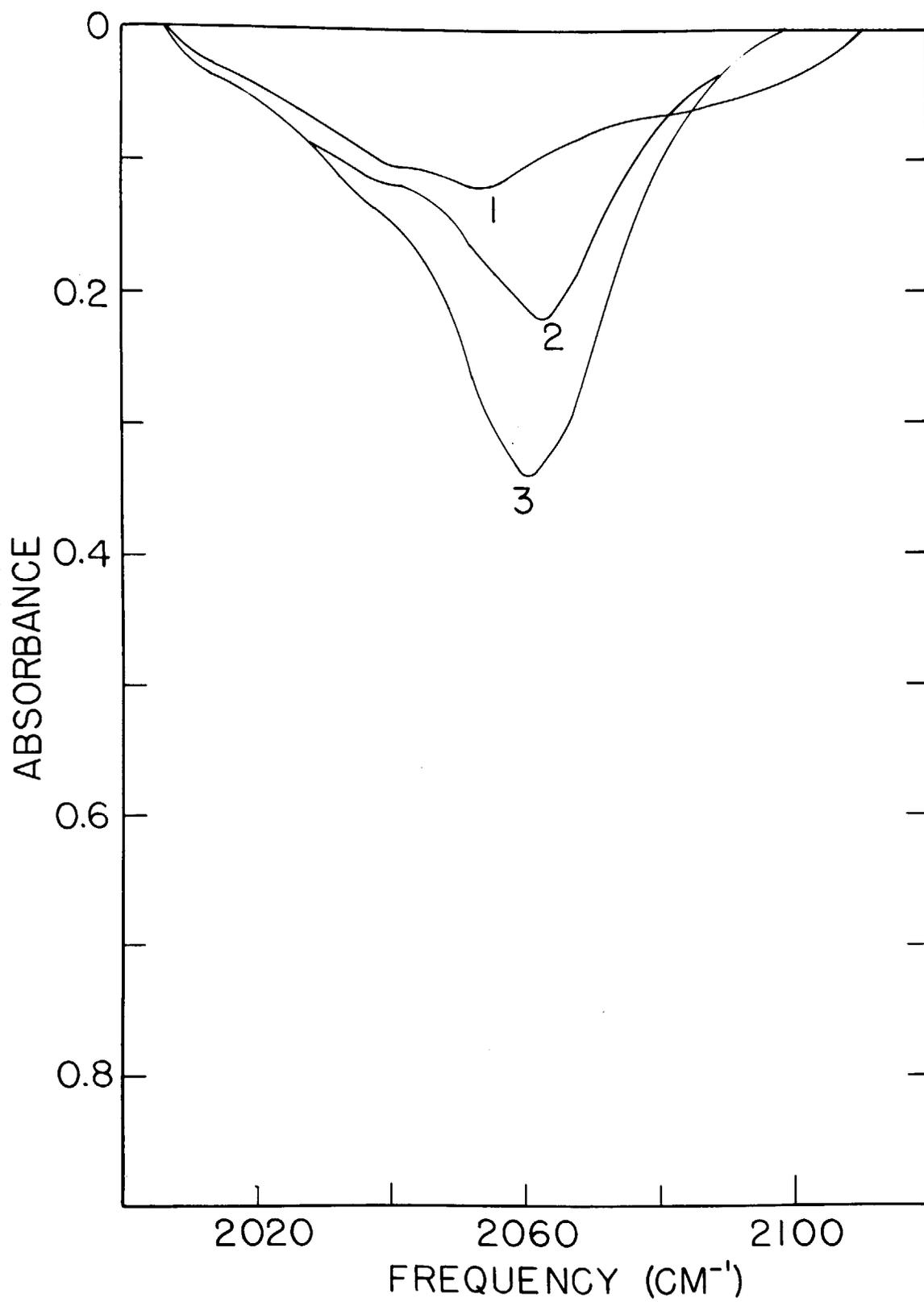


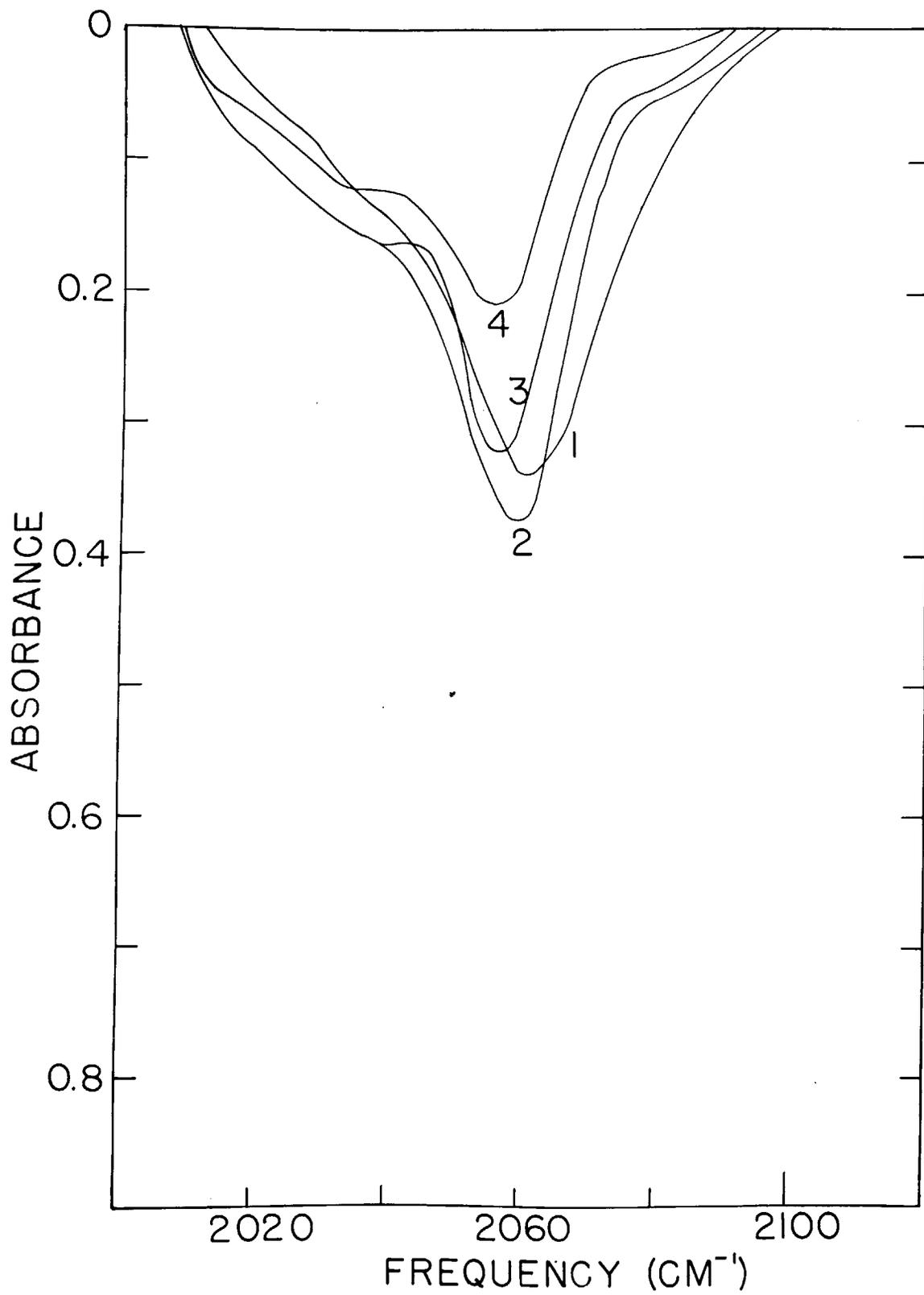
Figure XIX 1.5% Ni

Description of Hg Poisoned Sample

Sample No. C-522

Sample Weight 0.279 g

<u>Spectrum</u>	<u>CO Pressure</u>	<u>Treatment</u>
1	--	Exposed to Hg vapor for 29 minutes at $2 \times 10^{-3}$ mm
2	--	Pumped 20 minutes
3	--	Pumped 8 hours
4	--	Pumped 19 hours



and is shown again for convenience. Spectrum XIX-2 was obtained after 20 minutes desorption. The band has shifted to slightly lower frequency ( $2058 \text{ cm}^{-1}$ ) and the peak intensity has increased a small amount. Spectra XIX-3 and XIX-4 resulted after 8 hours and 19 hours desorption respectively. Here the sharp band disappears slowly at a constant frequency of  $2056 \text{ cm}^{-1}$ .

The sample was then desorbed 12 hours more for a total of 31 hours and very little change was noted from Spectrum XIX-4. At this stage Hg vapor was admitted at about  $2 \times 10^{-3}$  mm pressure for 2 hours. The spectrum did not change from XIX-4, indicating that all of the CO now present on the sample is completely influenced by the Hg originally added.

M. Adsorption of CO on a 1.5% Ni Sample Containing Preadsorbed Mercury

All of the previous experiments devised to study the Hg poisoning effect have had in common the approach of adding Hg to a surface already containing adsorbed CO. In order to see if the order of addition of these two gases was important, the reverse procedure was tried. A 1.5% Ni sample was exposed to Hg vapor at  $2 \times 10^{-3}$  mm for 2 hours and CO was then adsorbed in a stepwise fashion. Figure XX shows the results of this experiment. Spectrum XX-1 was obtained at a CO pressure of about  $1.5 \times 10^{-3}$  mm. A sharp band with maximum absorbance at  $2055 \text{ cm}^{-1}$  is present. Spectrum XX-2 represents the situation at a CO pressure of  $4.35 \times 10^{-2}$  mm; the

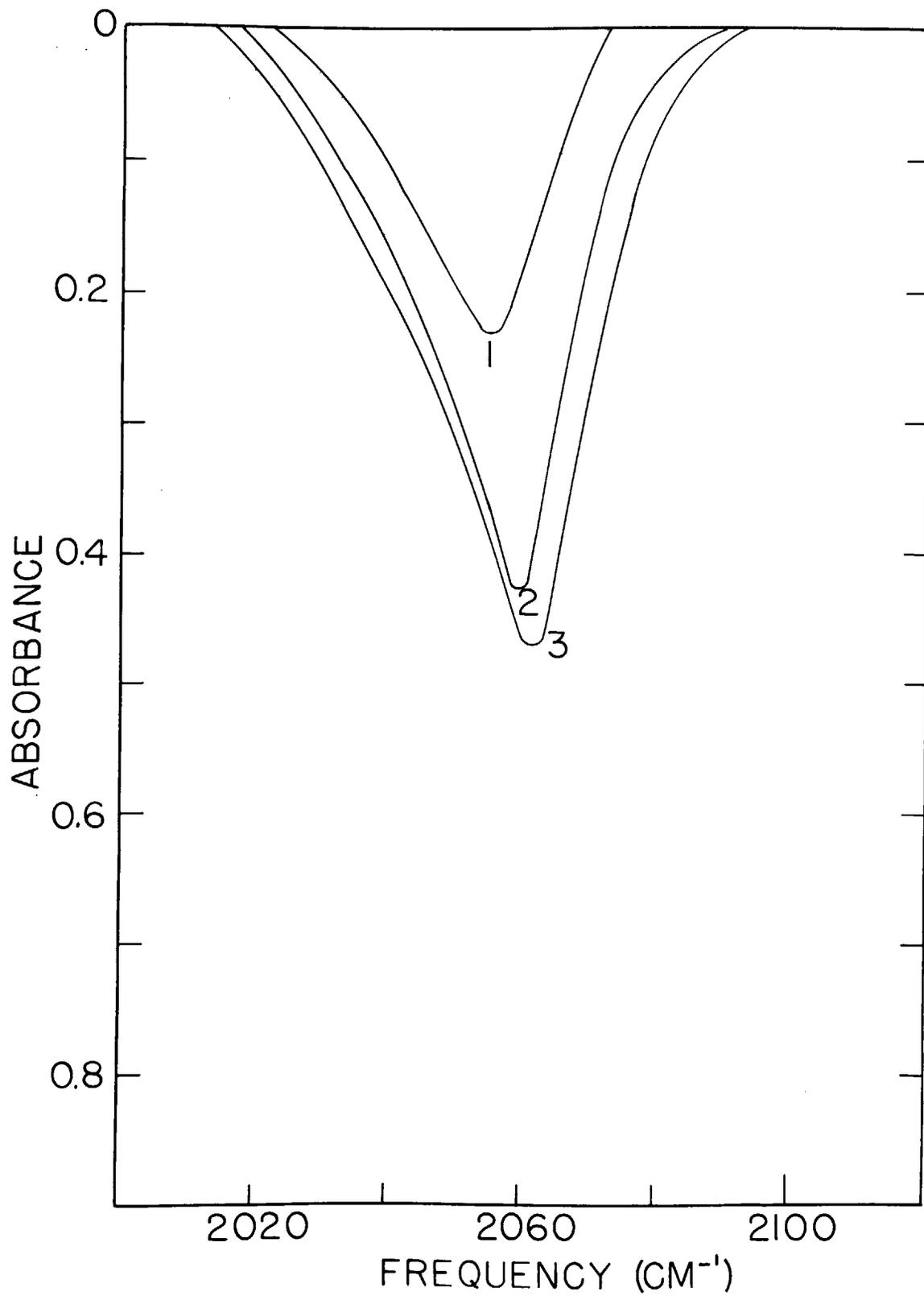
Figure XX 1.5% Ni

Adsorption of CO on Hg Prepoisoned Sample

Sample No. C-534

Sample Weight 0.285 g

<u>Spectrum</u>	<u>CO Pressure</u>	<u>Treatment</u>
1	$1.5 \times 10^{-3}$ mm	Exposed 2 hours to Hg vapor at $2 \times 10^{-3}$ mm; add CO.
2	$4.35 \times 10^{-2}$ mm	--
3	0.55 mm	--



sharp band has increased in absorbance and the absorbance maximum is now at  $2059 \text{ cm}^{-1}$ . Spectrum XX-3, taken at a CO pressure of 0.55 mm has grown only slightly greater than XX-2 in intensity and the band maximum has shifted to  $2061 \text{ cm}^{-1}$ .

The total uptake of CO per gram of Ni in this Hg prepoisoned sample is approximately  $3/4$  that observed on the unpoisoned samples shown in Figures XVI and XVII, all being compared at about the same CO pressure,  $4.7 \times 10^{-2}$  mm.

#### N. Spectrum of $\text{Co}(\text{CO})_3\text{NO}$

Because of the possibility that band E represented a precursor to  $\text{Ni}(\text{CO})_4$ , it seemed appropriate to determine the infrared spectrum of a compound which perhaps would approximate the structure of a possible  $\text{Ni}(\text{CO})_4$  precursor (i.e., surface species with 3 CO molecules bonded to a single Ni).

$\text{Co}(\text{CO})_3\text{NO}$  is isoelectronic with  $\text{Ni}(\text{CO})_4$ . The unshared electron of the NO is donated to the cobalt, making it pseudo-nickel. The compound is a gas at normal temperatures and is easily prepared.<sup>21</sup>

An infrared cell with  $\text{CaF}_2$  windows was used to contain this compound for spectroscopic examination. Figure XXI shows the spectrum obtained with the gas at successively lower pressures. Spectrum XXI-1, taken at the highest pressure shows a strong doublet in the  $2020 - 2120 \text{ cm}^{-1}$  range, and a weak band at  $2012 \text{ cm}^{-1}$  which displays rotational PQR fine structure. On lowering the gas pressure, the

Figure XXI

$\text{Co}(\text{CO})_3\text{NO}$  gas (slit = 0.2 mm)

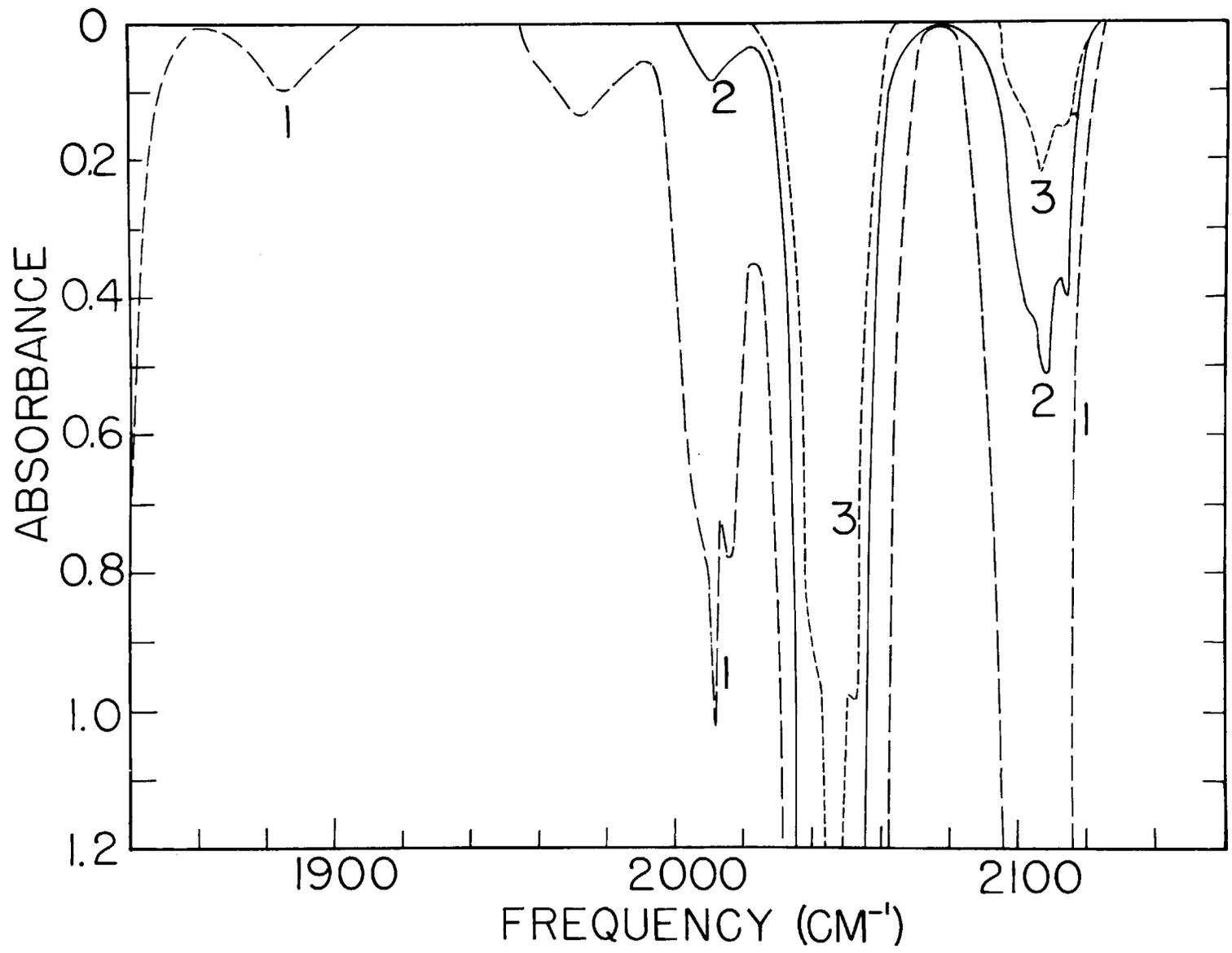
Spectrum

1

2

3

} taken at successively lower pressures



intensity of the higher frequency component of the doublet has been reduced to the point where PQR structure is discernable, (Q branch at  $2108\text{ cm}^{-1}$ ), while the lower frequency component is still too intense for the fine structure to be seen, (Spectrum XXI-2). Finally, Spectrum XXI-3 shows the situation at a still lower pressure. Here the PQR fine structure of the lower frequency component of the doublet is evident with the Q branch being at  $2047\text{ cm}^{-1}$ . The ratio of intensity of absorbance of the  $2108\text{ cm}^{-1}$  band to the  $2047\text{ cm}^{-1}$  band is about 1:6. This spectrum agrees in this region with a spectrum reported by Magee who obtained bands at  $2107\text{ cm}^{-1}$ ,  $2047\text{ cm}^{-1}$ , and  $2011\text{ cm}^{-1}$ .<sup>22</sup>

#### IV. DISCUSSION

The infrared spectrum of CO chemisorbed on a nickel surface has been reported previously by Eischens, Pliskin and Francis.<sup>7</sup> In their work the nickel was supported on non-porous silica, and the sample contained about 8% Ni by weight. A single desorption experiment was carried out; at full coverage infrared absorption bands were observed at 2075  $\text{cm}^{-1}$ , 2040  $\text{cm}^{-1}$ , 1930  $\text{cm}^{-1}$ , and 1852  $\text{cm}^{-1}$ . This result is in general agreement with our full - coverage spectrum of CO chemisorbed on a 10% Ni sample supported on alumina (see Figure III page 26) except that our A and B bands are about 40  $\text{cm}^{-1}$  higher in frequency than Eischens' comparable bands.

Bands above 2000  $\text{cm}^{-1}$  have been assigned by Eischens to species with the CO bonded to a single Ni atom, as in  $\text{Ni}(\text{CO})_4$ , and this type of bonding is designated as linear. Bands below 2000  $\text{cm}^{-1}$  are assigned to species with the CO bonded between Ni atoms in a bridge fashion. This generalized assignment is made on the basis that the linear carbonyl groups of metal carbonyls<sup>23</sup> and their derivatives<sup>24</sup> absorb in the range 1988 - 2080  $\text{cm}^{-1}$ , while metal carbonyls containing bridging CO groups have carbon-oxygen stretching frequencies below 2000  $\text{cm}^{-1}$ <sup>23</sup> (1828 - 1860  $\text{cm}^{-1}$ ). The general assignment made by Eischens has been adopted in the work reported here.

It should be noted that the analogy in frequencies between metal carbonyls and chemisorbed CO is good for

linear species (regions C, D and E lie at 2035, 2057, and 2082  $\text{cm}^{-1}$ , respectively) but poor for bridge species (regions A and B lie at 1915 and 1963  $\text{cm}^{-1}$ , respectively). This discrepancy is to be expected since the frequency is a function of the angle between the carbon-metal bonds of bridge carbonyl groups;<sup>25</sup> the frequency of the bridge species should therefore be sensitive to the interatomic distance of the Ni atoms, and this distance would not be expected to be the same as the metal-metal distance in metal carbonyls.

A. Interpretation of Results for Unpoisoned Ni Samples

The full-coverage spectra of CO adsorbed on surfaces containing supported Ni at various concentrations clearly show that the character of the Ni surface is a function of the Ni concentration (compare Figures III p. 26, VII p.33, and X p. 39). On a 1.5% Ni surface the bands at full coverage in regions A, B, and C are of low intensity relative to the bands in region D and E. When the concentration of Ni is increased to 10%, the bands in regions A, B, and C become pronounced. On a 25% Ni sample at full coverage the bands in regions A, B, and C are developed still more while the relative intensity in region E is decreased. The stripping experiment (Figure XI p.41) confirms the observation that Ni concentration affects the full coverage spectra. Bands A, B, and C seem to disappear simultaneously when the Ni atoms are slowly removed from the 10% Ni surface as  $\text{Ni}(\text{CO})_4$  gas, producing a final situation resembling that

obtained with 1.5% Ni samples at full CO coverage.

This fact that the bands in regions A, B, and C are strongest on the higher concentrated Ni samples suggests that these bands represent CO molecular species adsorbed on compact Ni sites. These sites will be designated "crystalline". Thus band A is assigned to a bridge CO species on crystalline Ni while band C is assigned to a linear CO species on crystalline Ni. The presence of crystalline sites on a 25% Ni sample is supported by the X-ray diffraction pattern which shows three broad lines corresponding to Ni crystals approximately  $40 \text{ \AA}$  in size. The fact that these lines were not evident on a 10% Ni sample may be caused by reduction of the average crystal size to an undetectable value; the absence of these lines may also be due to the necessarily lower number of Ni atoms which are available to scatter X-rays in the 10% Ni sample.

Bands A and C both develop at very low equilibrium pressures. With increasing coverage band C seems to intensify at constant frequency ( $2035 \text{ cm}^{-1}$ ), indicating that interaction between adsorbed linear CO's of this type at low coverage is small.

On the 1.5% Ni samples it is reasonable that the Ni should be of a more dispersed character. The predominance of the bands in regions D and E at full coverage suggests that these bands correspond to linear CO's bonded to Ni atoms which are more dispersed than those in crystalline sites. It is proposed that 10% and 25% Ni surfaces have a partial



This species would form only on crystalline sites during the later stages of the adsorption of linear species (band C), agreeing with the order of appearance of band B.

The band which forms at relatively high CO pressure in region E could possibly be due to the formation of some type of multiple CO species as suggested by other workers.<sup>7</sup> A  $\text{Ni}(\text{CO})_4$  decomposition experiment was designed to detect any tendency toward formation of multiple CO species during early stages of the formation of the band in region E. Decomposition of  $\text{Ni}(\text{CO})_4$  gas on freshly reduced 10% Ni samples initially liberates CO which is chemisorbed in the usual fashion as indicated by the initial stepwise spectra in Figure V (p. 30). At later stages of the decomposition however, extensive growth of a band in the D - E region occurs. This indicates that the decomposition of  $\text{Ni}(\text{CO})_4$  gas produces a Ni surface with a highly dispersed character, and in the later stages, these dispersed Ni atoms retain linear CO species.

Two recent independent determinations of  $\Delta F_{298.16}^\circ$  for the reaction:  $\text{Ni}(s) + 4 \text{CO}(g) = \text{Ni}(\text{CO})_4(g)$  give  $\Delta F_{298.16}^\circ = -5.4$  kcal and  $-5.8$  kcal.<sup>26</sup> These data give approximately,  $K_p_{298.16} = 10^4 \text{ atm}^{-3}$ . Qualitative data from our experimental studies indicate that it is possible to detect spectroscopically a  $\text{Ni}(\text{CO})_4$  pressure of about  $6 \times 10^{-3}$  mm in the cell used for studying the decomposition of  $\text{Ni}(\text{CO})_4$  gas by a 1.5% Ni surface. From the equilibrium constant it is found that the equilibrium CO pressure at which barely

detectable pressure of  $\text{Ni}(\text{CO})_4$  gas should be present would be about 4 mm CO. Actually unreacted  $\text{Ni}(\text{CO})_4$  gas was detected when the CO pressure reached about 1 mm. This indicates that equilibrium was not achieved, and that growth of the band in region E would have continued further without generating the barely detectable  $\text{Ni}(\text{CO})_4$  pressure if longer times had been allowed for equilibration. The additional fact that 3 CO gas molecules are generated for each  $\text{Ni}(\text{CO})_4$  molecule decomposed as band E grows (Figures VIII p. 36 and IX p. 37) indicates that band E in its early stages of development corresponds to a single linear CO adsorbed on a Ni atom which exists in a dispersed environment. The fact that the frequency of band E does not change appreciably as large amounts of  $\text{Ni}(\text{CO})_4$  gas are decomposed (Figure V p. 30, 10% Ni sample) suggests that it corresponds to a single linear CO bonded to a dispersed Ni at all stages of its growth.

Additional evidence for the assignment of band E as a single linear CO is given by comparison of its frequency ( $2082 \text{ cm}^{-1}$ ) with the vibrational spectra of  $\text{Ni}(\text{CO})_4$  gas and  $\text{Co}(\text{CO})_3\text{NO}$  gas. A recent interpretation of the spectrum of  $\text{Ni}(\text{CO})_4$  gas assigns the two CO stretching fundamentals as follows:<sup>27</sup>

(IR)	$\nu_5 = 2057 \text{ cm}^{-1}$	asymmetric CO stretch
(Raman)	$\nu_1 = 2128 \text{ cm}^{-1}$	symmetric CO stretch
also,	(IR) $\nu_{\text{C}^{13}\text{O}} = 2018 \text{ cm}^{-1}$	( $A_1$ , $C_{3v}$ ; isotope band due to $\text{C}^{13}$ present in $\text{Ni}(\text{CO})_4$ gas at its natural abundance of 1.1%).

The fact that band E is a single band indicates that it is not associated with a multiple CO species since two or more CO's per nickel atom would produce a double band due to symmetric and asymmetric CO stretching vibrations. This interpretation is further substantiated by the fact that the frequency of band E lies between the symmetric and asymmetric vibrational frequencies of  $\text{Ni}(\text{CO})_4$  gas.

Additional evidence for this assignment is furnished by the spectrum of  $\text{Co}(\text{CO})_3\text{NO}$  gas. An analysis of the spectrum of this compound has been made<sup>22</sup>, but does not seem valid in the light of the recent interpretation of  $\text{Ni}(\text{CO})_4$ . Because  $\text{Co}(\text{CO})_3\text{NO}$  has  $C_{3v}$  symmetry, both the asymmetric and symmetric CO stretching frequencies are infrared active. The frequencies observed are:

IR (very strong)	2047 $\text{cm}^{-1}$
IR (strong)	2108 $\text{cm}^{-1}$
IR (medium)	2012 $\text{cm}^{-1}$

It seems quite reasonable to assign the fundamentals by analogy with the  $\text{Ni}(\text{CO})_4$  assignment. The band at 2012  $\text{cm}^{-1}$  has been assigned as the symmetric CO stretch by Magee.<sup>22</sup> Both its position and intensity suggest however that this band is really the  $\text{C}^{13}$  isotope band, and this is supported by the analogous  $\text{Ni}(\text{CO})_4$  assignment. The two strong bands at 2047  $\text{cm}^{-1}$  and 2108  $\text{cm}^{-1}$  would then represent the asymmetric and symmetric CO stretch, comparing favorably with the  $\text{Ni}(\text{CO})_4$  assignment. It is evident that band E for CO ad-

-sorbed on Ni lies between these two bands, again supporting the interpretation that band E corresponds to a single linear CO on a dispersed Ni atom.

Band D is the most difficult band to observe accurately because of its position between C and E on concentrated samples. Both its frequency ( $2057\text{ cm}^{-1}$ ) and order of appearance on stepwise adsorption of CO on both 10% and 1.5% Ni samples suggest that it corresponds to a linear CO adsorbed on a Ni site which is intermediate in character between crystalline and dispersed sites. This particular intermediate type of surface is designated "semicrystalline." Band D will be discussed further in connection with the mercury poisoning studies.

Extensive desorption at room temperature indicates that the various species formed by adsorption of CO are desorbed in essentially the reverse order in which they were formed; also, desorption at room temperature is reversible in the sense that CO may be re-adsorbed back to full coverage after lengthy desorption. This indicates that there is no decomposition of CO to give carbides on the surface during desorption at room temperature.

An unreduced NiO sample showed no adsorption of CO at room temperature, and no infrared bands due to adsorbed CO species could be detected, so that it is certain that the adsorbed species reported are really on a Ni surface. This is further supported in the case of the species giving band E, since it may be produced by the decomposition of  $\text{Ni}(\text{CO})_4$ .

gas.

The adsorption of CO on crystalline Ni sites occurs at very low pressure and is comparable to normal chemisorption. Adsorption of CO on semicrystalline and dispersed sites occurs at pressures higher than those normally associated with chemisorption.

To summarize the following correspondence between infrared adsorption bands and adsorbed species is proposed:

BAND	FREQUENCY $\text{cm}^{-1}$	SPECIES	SITE	STRENGTH of ADSORPTION
A	1915	$\begin{array}{c} \text{O} \\   \\ \text{C} \\ / \quad \backslash \\ - \text{Ni} - \text{Ni} - \end{array}$	crystalline Ni	very strong
B	1963	$\begin{array}{c} \text{O} \ \text{O} \ \text{O} \\   \   \   \\ \text{C} \ \text{C} \ \text{C} \\ / \ \backslash \ / \\ - \text{Ni} - \text{Ni} - \end{array}$	crystalline Ni	moderately strong
C	2035	$\begin{array}{c} \text{O} \\   \\ \text{C} \\   \\ - \text{Ni} - \end{array}$	crystalline Ni	very strong
D	2057	$\begin{array}{c} \text{O} \\   \\ \text{C} \\   \\ - \text{Ni} - \end{array}$	semi- crystalline Ni	moderately strong
E	2082	$\begin{array}{c} \text{O} \\   \\ \text{C} \\   \\ - \text{Ni} - \end{array}$	dispersed Ni	weak

B. Interpretation of Results for Mercury Poisoning of the Nickel Surface

On Hg free samples in the C - D - E region there is an inverse relationship between the CO stretching frequency and the strength of the Ni-C bond. The most weakly held linear CO species has the highest frequency (band E), while the most strongly held species has the lowest frequency (band C). Since stepwise adsorption of CO at low coverage results in the growth of a band in region C at constant frequency, the resulting band most probably represents a CO species adsorbed on homogeneous Ni sites; these sites have been designated crystalline. Likewise during the final stages of stepwise adsorption, the band in region E grows at constant frequency and has been interpreted as resulting from linear CO species adsorbed on dispersed Ni sites - these too must be of a homogeneous nature as reflected by the constant frequency at which band E forms.

It is reasonable to propose that the band in region D, caused by linear CO species adsorbed on semicrystalline Ni sites, should represent CO adsorption on a continuous distribution of Ni sites between the two extremes, crystalline and dispersed. That this is true is indicated in the desorption of the 25% Ni sample, where intensity loss in region D was always from the high frequency side of the band, i.e. the most dispersed of the semicrystalline sites show weakest adsorption of CO.

The studies made of the Hg poisoning of Ni sur-

-faces indicate that Hg poisoning causes crystalline sites to lose their ability to chemisorb bridged CO. Thus the Hg treatment of a 10% Ni sample at full CO coverage actually resulted in a continuous decrease in the intensity of bands attributed to bridge species (A and B) on crystalline sites. Also a 10% sample that has been Hg poisoned while being desorbed does not have the ability to re-adsorb CO as bridge species A and B.

It is also evident from the poisoning experiment on 10% Ni at full CO coverage that the dispersed Ni sites lose their ability to chemisorb CO (as band E) when Hg poisoning takes place. Since CO is weakly held by the dispersed Ni sites it is reasonable to suspect that Hg may easily displace these CO species.

The only sites which retain adsorbed CO in the presence of Hg are the semicrystalline Ni sites. These sites on a Hg-free sample retain adsorbed CO moderately strongly and the subsequent adsorption of Hg causes these sites to retain the preadsorbed CO more strongly; this is indicated by the extremely slow desorption rate after Hg poisoning. There is some evidence that the semicrystalline sites lose part of their ability to adsorb CO if they are poisoned with Hg before CO addition (compare Figure XVI p.53 and XX p.59) and it may be that lengthy prepoisoning of these sites will cause them to lose all their CO adsorptive capacity.

The most striking effect observed on Hg poisoning of the semicrystalline Ni sites is the resulting intensifi-

-cation of infrared absorption. A sharp, strong band appears at about  $2060 \text{ cm}^{-1}$ ; this will be referred to as band D\*. The intensity of this new band is proportional to the extent of Hg poisoning of the semicrystalline Ni sites; intensification ceases after lengthy exposure to Hg, presumably because all the semicrystalline sites which have an adsorbed CO have been affected by the presence of Hg. The position of the intense band, D\*, is not a function of the extent of Hg poisoning; the band intensifies at constant frequency during stepwise Hg poisoning of a 1.5% Ni sample containing preadsorbed CO species (band D). The absence of a frequency shift as D\* intensifies indicates that the Hg does not selectively poison a particular type of semicrystalline site in the continuum of semicrystalline sites extending from crystalline to dispersed Ni sites.

This viewpoint is supported by the experiment in which Hg was added to a 1.5% sample in sufficiently small amounts to cause only partial poisoning. The resulting band D\* was about one-half the maximum possible intensity (i.e. the intensity observed for complete Hg poisoning) and disappeared on desorption at about the same rate as the completely developed band on a fully poisoned surface.

If the effect of each Hg atom were to influence a large area of semicrystalline nickel surface (as in an explanation based on a band theory of metals) all adsorbed CO molecules would be equivalent and would become more strongly held and more intensely infrared absorbing as more

Hg was added. Then at an intermediate stage of poisoning band D\* should disappear on desorption more rapidly than it does after complete poisoning; this is not observed. Also after a period of desorption of a partially poisoned sample, further poisoning should continue to make band D\* grow; this is not observed. But if the effect of a Hg atom is local, then at an intermediate stage of poisoning some adsorbed CO molecules are affected (converted to a new species which is more strongly held and has a greater absorbancy) while other CO's are not affected. Then one predicts that band D\* should disappear at the same rate for all stages of poisoning, as is observed. Also, a period of desorption on a sample which has been partially poisoned will remove most of the weaker held CO species which had not been affected by Hg (band D species). Then further Hg poisoning cannot cause band D\* to grow, again in agreement with observation.

Thus the effect of the Hg seems to be of a local nature, and extensive poisoning does not seem to cause a situation which is very different from that caused by slight poisoning, with the exception that the intensity of band D\* (and also the number of CO's on sites affected by Hg) is proportional to the extent of poisoning.

Since the position of band D\* may be varied between the limits  $2070\text{ cm}^{-1}$  and  $2050\text{ cm}^{-1}$  by adsorption and desorption of CO (see Figure XIII p. 47), it is plausible that the continuous distribution of semicrystalline Ni sites

between the two extremes, crystalline and dispersed, is unaltered by Hg poisoning. Furthermore since the position of band D\* is observed to shift to higher frequency upon adsorption of CO rather than to increase in absorbance only on the high frequency side; it is plausible to suggest that some displacement of Hg may take place when CO is adsorbed, and this Hg may re-enter the Ni "lattice" upon desorption of CO (since the band shifts in the opposite fashion to lower frequency). This type of effect is particularly evident in the 10% Ni sample which was extensively poisoned at full CO coverage. Here band D\* did not develop completely until desorption of some of the weakly held CO had taken place; band D\* was then observed to shift to lower frequency and to increase in absorbance at the maximum. Alternately, the shifting effect could be explained by postulating that interactions between adsorbed linear CO molecules causes shifting of the band frequency as coverage varies.

It has been shown that the Hg poisoning effect does not depend on the preadsorption of CO on the semi-crystalline Ni sites, since the order of adsorption of Hg and CO is not important to achieving the effect -- a strong band is produced in both cases. Thus this Hg poisoning of semicrystalline sites may be visualized as a local alloying process in which the Hg enters into the semicrystalline Ni lattice, perhaps at vacancies which are certainly very prevalent in the semicrystalline surface. In this connection, Eischens<sup>29</sup> has reported a spectrum of CO adsorbed on a Cu-Ni

alloy (10% Cu) which shows a band in the linear CO region which has a greater relative intensity compared to the bridge CO bands than the linear CO band on a pure Ni surface.

In summary, Hg poisoning causes the appearance of a new more intense band (D\*). The new band is associated with a linear CO species strongly absorbed on a semicrystalline site which is "alloyed" with Hg. The effect of Hg is of a local nature as far as its influence on chemisorbed CO is concerned.

### C. Considerations on Bonding

Several major difficulties are inherent in the spectroscopic approach employed in this problem. The entire study of the adsorbed CO species is based on observations of the stretching frequency of the carbon-oxygen bond; this bond is presumably not directly involved in the bond between CO and Ni. Therefore this bond may not be particularly sensitive to relatively large changes in the structure of the adsorbed CO species. In addition interpretation is made difficult by the fact that a definite molecular formula can not be assigned to the adsorbed CO species on the basis of quantitative chemical evidence. Also, the problem is further complicated by the presence of several CO adsorbed species on the surface whose relative concentrations are unknown. Thus the interpretation is to be considered tentative at the present stage of refinement.

It is possible to speculate about the nature of the bonding between Ni and adsorbed CO. The fact that two

very different molecular species (linear and bridge) form on crystalline Ni indicates that heterogeneity of the crystalline surface may be the factor which determines whether a particular CO molecule is adsorbed as a linear or a bridge species. As stated in the introduction, the resonance structure proposed by Pauling<sup>2</sup> for bulk metallic Ni is intermediate between Ni A, with two unpaired electrons in atomic d orbitals, and Ni B with no unfilled atomic d orbitals. It is reasonable to assume that the resonance situation for Ni atoms in the crystal surface will be different from that in bulk Ni, and will vary with the degree of disperseness associated with the chemisorbing sites. This variation in the resonance hybridization is probably responsible for the two general types of adsorbed CO species - linear and bridge. Thus a site having a predominantly Ni A character is able to accept the two lone pair electrons from the CO, producing a linear CO species. Those sites which are more like Ni B may be able to accept only one electron from CO, thereby participating in the formation of a bridge CO species. As the number of nearest Ni neighbors decreases for the dispersed sites, presumably the number of unfilled atomic d orbitals per Ni atom increases, and this factor plus the geometric factor cause only linear CO species to be formed on adsorption.

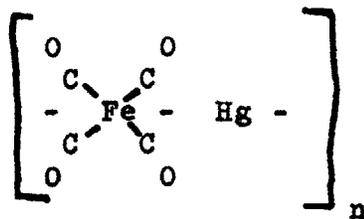
The Ni-C bond strength for linear CO species adsorbed by crystalline Ni is much stronger than the same bond for CO adsorbed on dispersed Ni. This is indicated by the low CO equilibrium pressure and the extremely slow rate

of desorption of the C species. The dispersed Ni-CO species probably have Ni-C bond strengths comparable to that observed for Ni(CO)<sub>4</sub>, about 35.2 kcal. per Ni-C bond.<sup>30</sup> At present there seems to be no theoretical justification for the decrease in Ni-C bond strength in the linear adsorbed species as the Ni becomes more dispersed. It is possible that the influence of the alumina support comes into play in the case of the dispersed Ni sites. This work does not differentiate the effect of the support from the effect of dispersion of Ni atoms.

It is impossible to advance more than conjecture concerning the mercury poisoning effect. Two experimental facts are prominent: (1). Hg adsorbed on semicrystalline Ni causes the Ni-C bond strength in adsorbed linear CO species to increase markedly. (2). The extinction coefficient for the CO stretching vibration in adsorbed linear CO species on semicrystalline Ni sites is increased several fold when Hg poisoning of the Ni surface takes place.

It is possible that the first of the two effects is caused by an increase in the number of metallic bonding orbitals which are utilized by a Ni atom in a semicrystalline site when Hg poisoning takes place. This view is supported by the existence of various Hg-metal carbonyl complexes which are much more stable than their parent carbonyls. It has been proposed on the basis of chemical evidence alone that some of these compounds are actually polymeric; a possible structure for a mercury - iron carbonyl polymeric

complex is:<sup>23</sup>



The increase in the carbonyl extinction coefficient for poisoned Ni surfaces containing adsorbed CO is probably caused by changes in the electronic structure of the adsorbed CO species which are not related to the C - O bond strength. Some examples of this type are known in chemical compounds; in "the series CHX<sub>3</sub>, chloroform, bromoform, and iodoform there is little change in the C-H bond stretching frequency, but its intensity increases some four fold."<sup>31</sup>

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