PREFACE

Boron trifluoride is known to enhance the catalytic activity of oxides in various reactions. Several authors have attempted to study the infrared spectra of BF_3 treated silica and from their results, it has been assumed that possibly BF_3 is physically adsorbed on this oxide. Boron trichloride has been used to study the surface properties of silica. Although it has been proposed that BCl_3 is adsorbed on silica, no spectroscopic evidence have been presented to date. This work was undertaken to investigate, by infrared spectroscopic techniques, the mechanisms of BF_3 and BCl_3 adsorption processes on silica and the nature of the surface species produced on adsorption.

ACKNOWLEDGEMENT

This research was conducted under the direction of Dr. B.A. Morrow without whose patience and guidance it could not have been carried to a successful conclusion. I am also grateful for the interest shown and the assistance provided by Dr. Morrow in the shaping of this thesis. I wish to thank the National Research Council of Canada and the Ontario Department of University Affairs for the financial assistance.

Thanks are also due to Mrs. Micheline Côté for typing this thesis. To my parents, I wish to express a sincere gratitude for their constant moral support and encouragement.

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ABSTRACT

An infrared spectroscopic study of the adsorption of BF_3 and BCl_3 on silica has been carried out. The silica samples were dehydrated under vacuum at various temperatures from 400-1020°C before admitting the adsorbate to the reaction cell and the nature of surface species produced depended on this pretreatment temperature.

Upon adsorbing BF_3 on a silica sample that had been previously evacuated at temperatures below 1000°C, a set of bands were produced which were replaced by a new set of bands on evacuation. Similar results were observed with BCl_3 treated silica. However, during this evacuation, a growth of the 3749 cm^{-1} Si-O-H band was observed after BF_3 adsorption but a corresponding growth of the 3700 cm^{-1} B-OH band was observed after BCl_3 adsorption. Further, the initial set of bands, produced on adding BF_3 to silica samples which had been previously dehydrated at temperatures above 1000°C were extremely stable to evacuation, whereas the corresponding bands with BCl_3 were again replaced on evacuation.

A mechanism is proposed that would explain the observed results. Some of the features of this mechanism are:

1. BX_3 (X=F, Cl) initially reacts with the surface hydroxyls to give Si-O-BX_2 type species.
2. On evacuation, these groups further react to give the Si-O_2-BX type species.

3. A small amount of 'H_2O' is available to the surface during evacuation and this 'H_2O' reacts with the BX_3 treated surface to refurnish Si-O-H groups.

4. However, the Si-O-BCl_2 and the Si-O_2-BCl groups further react with this 'H_2O' to give Si-O-B-$(OH)_2$ and Si-O_2-B(OH). It has been shown that both BF_3 and BCl_3 are chemically adsorbed on silica evacuated at very high temperatures. It has been proposed that on these surfaces, various other active sites, for example Si-O· radicals and Si-O-Si bridges are possibly present.

An attempt has been made to study the bands due to BO_2 symmetrical stretching modes in the 1200 cm^{-1} region by adsorbing BX_3 on various other oxides, e.g. Al_2O_3, TiO_2, MgO and ZnO.

It has been shown that the surface silanols exchange with H_2O^{18} at elevated temperatures and a maximum 70% exchange has been obtained at 400°C. A new band present at 3738 cm^{-1} is assigned to the OH stretching mode of Si-O^{18}-H. Using the O^{18} exchange technique it has been possible to assign surface adsorbate stretching modes arising from species of the type Si-O-BX_2.

INTRODUCTION

In the bulk of a material, the attractive forces on a particular atom are cancelled out by the forces on the neighboring atoms. However, the atoms at the surface are no longer equally surrounded by adjacent atoms and the absence of these neighboring forces produces a strain or unsaturation on the surface which is relieved either by the rearrangement of the surface bonds or groups, as is done in annealing, or by the adsorption of other molecules. The molecule adsorbed is known as the adsorbate and the material on which it is adsorbed is the adsorbent.

The free energy change ΔG can be expressed in terms of the heat of adsorption ΔH and the entropy change ΔS

$$\Delta G = \Delta H - T\Delta S$$

where T is the absolute temperature. Adsorption is a spontaneous process and is accompanied by a decrease in the free energy ΔG. In most cases, the entropy is also lowered on adsorption since the adsorbed molecules have fewer degrees of freedom on the surface than in the gas phase. The resultant value of ΔH becomes negative so that adsorbtion is generally an exothermic process.

There have been a large number of investigations of the reactions of gases on solid surfaces because of the ability of these surfaces to selectively catalyse chemical reactions. Both physical and chemical adsorption can take place on solid surfaces and in many cases a clear distinction can be made

between these two processes. Physical adsorption is a rapid process and usually occurs at temperatures near the boiling point of the adsorbate. Chemisorption (chemical adsorption) frequently requires temperatures higher than those effecting physical adsorption and longer periods of contact. The heats of physical adsorption are usually below 10KCal/mole whereas those of chemisorption are generally above 10KCal/mole. However, the heat of chemisorption can also be very low, for example, the heat of adsorption of atomic hydrogen on tungsten varies from 10-2.4KCal/mole depending on the percentage of surface coverage.[1] A further distinction is that physical adsorption may result in the formation of multilayers on the surface. However, since chemisorption involves chemical reaction between a surface site and the adsorbate molecule, only monolayer coverage is possible.

Infrared spectroscopy has been able to give additional information on the types of bonds formed on the surface and in many cases has been able to differentiate clearly between physical and chemical adsorption. For example, it has been found that the spectrum of a physically adsorbed molecule does not change very much from that of the gas phase spectrum whereas when a molecule is chemisorbed many of the bands in the gas phase spectrum of the adsorbate are replaced by a new set of bands on adsorption, suggesting the formation of new bonds. After adsorbing carbon dioxide on silica-supported

nickel[2] a band appears at 2345 cm^{-1}, which is close to the 2349 cm^{-1} band of gaseous CO_2. Two other bands are observed at 1615 and 1365 cm^{-1}. The 2345 cm^{-1} band due to physically adsorbed CO_2 disappears on evacuation at room temperature but the other two bands which are attributable to surface carbonates produced on chemisorption are stable to room temperature evacuation. This indicates that the surface forces involved in chemisorption are stronger than those effecting physical adsorption.

Since the frequencies and intensities of the infrared bands depend on the symmetry of the molecule and the electrical charge distribution within it, any rearrangement of the molecule due to surface forces produces a change in its spectrum. The surface forces present on physical adsorption are weak van-der-Waals type forces[3] and can perturb the symmetry of the adsorbate molecule only slightly so that the vibrational frequencies are shifted by about 1% relative to those of the gas phase molecule. The forces involved in chemisorption are capable of forming chemical bonds between the adsorbate molecules and reactive surface groups. These surface bonds may produce a set of infrared bands that have quite different frequencies from those of the absorbate in the gas phase.

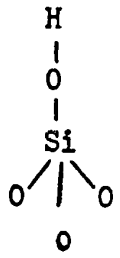
In certain cases, infrared spectroscopic techniques have not been effective in distinguishing between physical and chemical adsorption. On adsorbing carbon monoxide on

ZnO where it is generally assumed that chemisorption has taken place, a band at 2174 cm^{-1} is produced which is 31 cm^{-1} higher in frequency from the corresponding band at 2143 cm^{-1} produced by gaseous carbon monoxide. However on evacuation at room temperature the 2174 cm^{-1} disappears; this behaviour is characteristic of physically adsorped species.

In the last twenty years, the application of various other spectroscopic techniques for studying surface phenomena has made it possible to identify many adsorbed species. Ultra-violet spectroscopy [5] and electron spin resonance [6] have been able to identify complex surface species like carbonium ions, ion radicals and charge transfer complexes. Nuclear magnetic resonance spectroscopy has been applied to study the surface groups present on various oxides.

Silica and silica-alumina have been used extensively as catalysts and support materials for other catalysts and are highly amenable to infrared spectroscopic investigations because of their high surface area and low light scattering properties. Many of the early infrared studies on the process of adsorption has been carried out using silica.

Kiselev [8] first observed that most oxide surfaces, including silica, are covered to varying degrees with hydroxyl groups. Carman [9] concluded that the surface silicon atoms adsorb water in order to retain a tetrahedral coordination with oxygen atoms.



Shapiro and Weiss [10] attempted to determine the surface hydroxyl (or silanol) coverage by heating bulk silica at increasing temperatures and recording the weight lost due to dehydration. Iler [11] determined that silica gel aged at 155°C, has about 7.9 hydroxyl groups per 100 square A.

Terenin and Yaroslavsky [12] were first to observe the 3750 cm^{-1} fundamental band of Si-O-H and its overtone band at 7300 cm^{-1}. McDonald [13] studied the infrared spectra of a commercially available silica known as Cab-O-Sil in the 4000-2500 cm^{-1} region (Fig. 1). Before degassing, there was a sharp band at 3747 cm^{-1} and a broad band extending from 3700-3000 cm^{-1}. The later band has two distinct peaks at about 3520 and 3600 cm^{-1}, (Fig. 1a). On degassing at 27°C for 3 hours (Fig. 1b), the intensity of the broad band decreased and that of the 3747 cm^{-1} band increased. After degassing at 500°C for ½ hour (Fig. 1c), the broad band at 3520 cm^{-1} was removed and a slightly asymmetric 3747 cm^{-1} band accompanied by a tail that contained the 3660 cm^{-1} band was also present. On degassing at 940°C, (Fig. 1d), the 3660 cm^{-1} band was removed leaving a sharp symmetrical band at 3747 cm^{-1}. The 3747 cm^{-1} band was attributed to the O-H stretching vibrations of isolated single surface hydroxyl

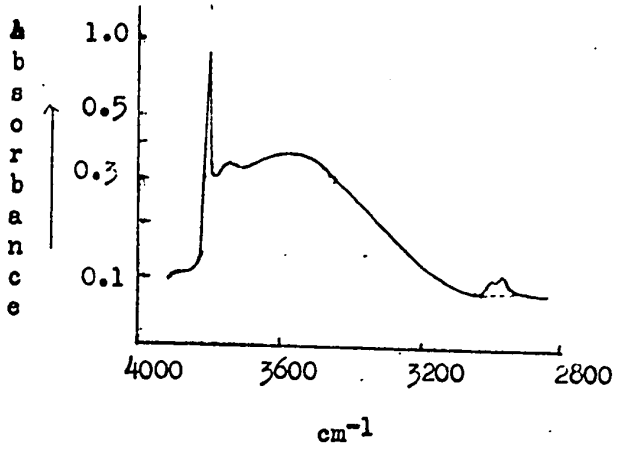


Fig.1-a. Before degassing

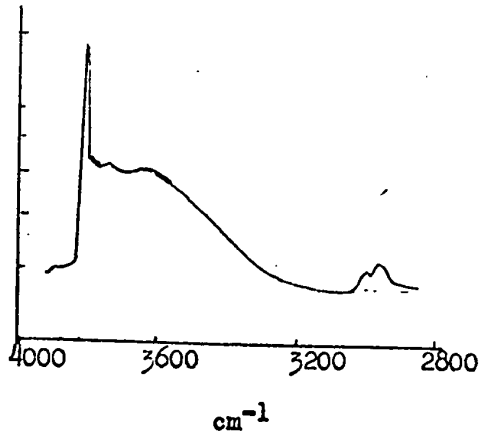


Fig. 1-b. Degassed 3 hr. at 27°C.

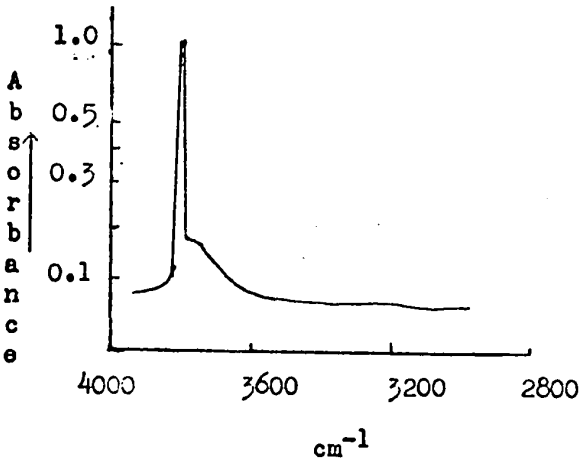


Fig 1-c. Degassed $\frac{1}{2}$ hr. at 500°C.

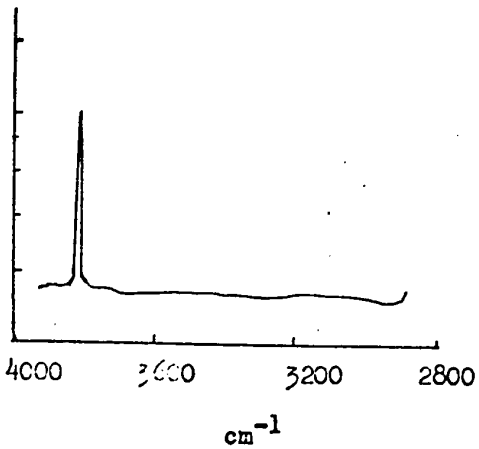
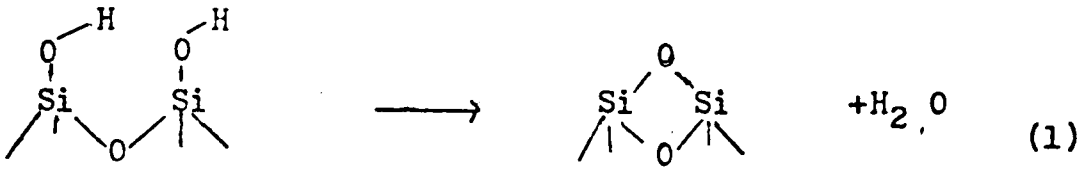


Fig. 1-d. Degassed 8 hr. at 940°C

Figure 1. Infrared spectra of Cab-O-Sil degassed at various temperatures.

groups. The broad band present before degassing was assigned to strongly hydrogen bonded silanols and physically adsorbed water. The later was removed on degassing at room temperature; the strongly hydrogen bonded surface hydroxyls contributing to the broad band were removed on evacuating the sample at 500°C. The 3660 cm^{-1} band was assigned to the stretching vibration of weakly hydrogen bonded silanols that could be removed on degassing at 940°C. McDonald further reasoned that the 3750 cm^{-1} Si-O-H band should also exhibit satellite bands due to the hindered rotation of the O-H groups. The absence of any such bands suggests that the Si-O-H bond angle may be a maximum of 180 degrees. However if the rotational modes interact with the lattice vibrations, the PR branches would not be resolved. In a recent paper, Peri [14] has reported the presence of weak PR branches on D_2O exchanged silica which were 200 cm^{-1} apart from the main 2760 cm^{-1} Si-O-D valence vibration band. From this data he calculated the Si-O-H bond angle to be 113 degrees.

Kiselev, [15] Fraissard[16] and Hockey and Pethica[17] have studied the dehydration and rehydration properties of silica with various methods. Kiselev [15] proposed that dehydration occurs via the following mechanisms:



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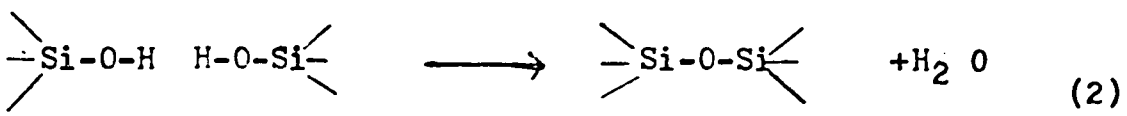
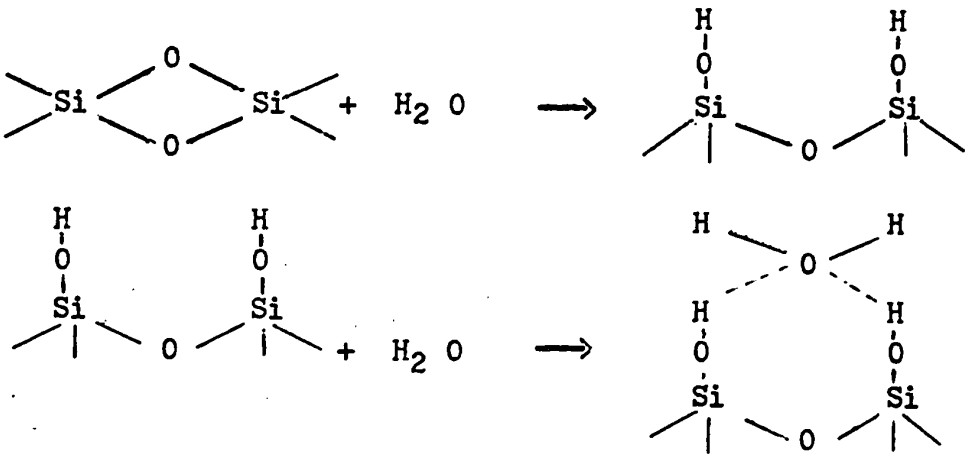


(2)

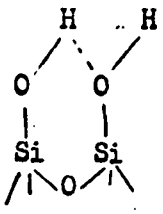
Reaction (1) involves the condensation of adjacent hydrogen bonded hydroxyls and reaction (2) causes sintering across pores. Both these reactions are reversible if carried out at temperatures below 400°C. The rehydration properties have been studied extensively by various workers.[13,18,19] Their data show that rehydration is possible on silica samples heated below 800°C via both chemisorption and physical adsorption of water. The silica surfaces heated above 800°C



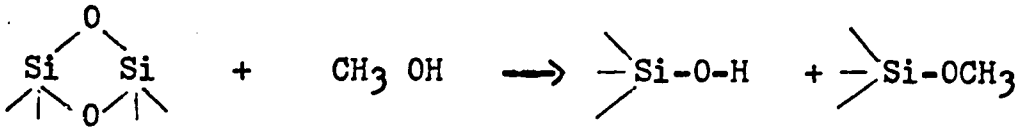
become hydrophobic and adsorb only small quantities of water. Above 900°C sintering starts and the surface area begins to decrease.

Following the identification of the surface silanols, a large amount of work was done to determine the nature and reactivities of the hydroxyl groups. Folman and Yates [20] have shown that surface hydroxyls can be esterified by alkyl or aryl alcohols;

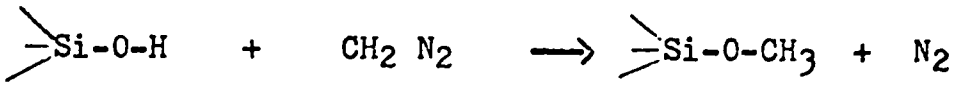
Sidorov [21] further showed that single O-H groups are more reactive than the hydrogen bonded vicinal hydroxyls which have the following structure:



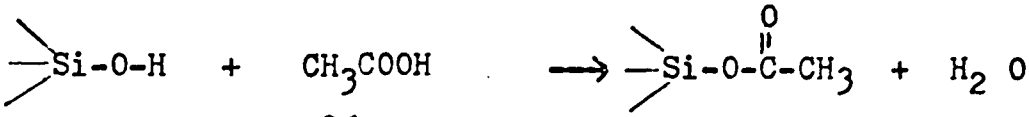
Methanol is also chemisorbed [22] on high temperature heated silica surfaces. The Si-O-Si bridge reacts to produce a hydroxyl and methoxy group:



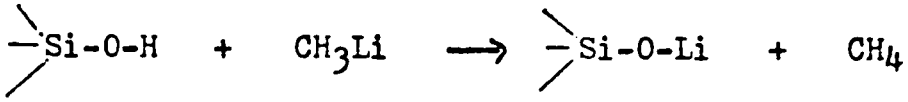
In the absence of water, diazomethane [3] reacts with a surface hydroxyl to produce a methoxy group.



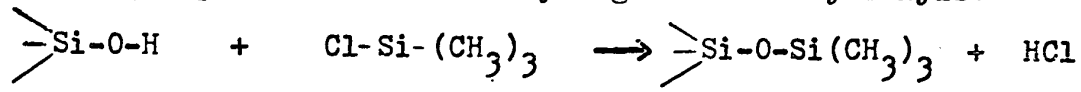
Cant and Little [24] have reported that ammonia can be adsorbed after long contact with the silica surface. The acidic hydroxyl groups present on silica-alumina surfaces react with carboxylic acids and carboxylic acid derivatives:



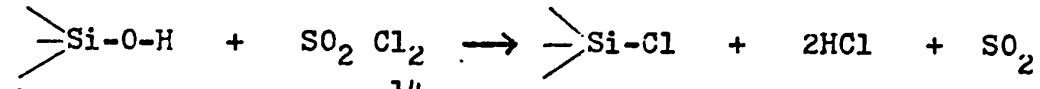
Some alkyl lithium [25] reagents also react with surface hydroxyl groups:



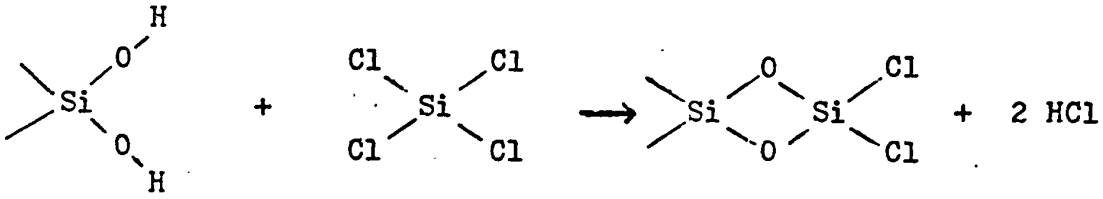
The reaction of organo silicon compounds with the silanols has been used to deactivate the surface by removing the H atom present on the hydroxyl group. For example, trimethyl chlorosilane [26] reacts with silica at 150°C, the reaction taking place preferentially with the single hydroxyl groups instead of the hydrogen bonded hydroxyls:



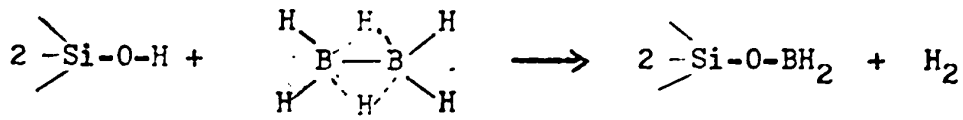
Because surface hydroxyls are weakly acidic, they can be replaced by halogens. Porous glass surfaces can be fluorinated with 30% solution of ammonium fluoride. [28] The surface hydroxyls can be chlorinated by reacting with sulfuryl chloride: [29]



Silicon tetrachloride [14] reacts with silanol groups via the following reaction:



To distinguish between the surface hydroxyl groups and physisorbed water bands, Shapiro and Weiss [10] first studied the adsorption of diborane on silica. Their proposed mechanism was:



Later investigations[30,31,32] indicate that this method cannot be used and that a variety of products are possibly present on the surface.

Silica surface hydroxyls are found to exchange with D_2O with a total replacement of the 3750 cm^{-1} Si-O-H band by a 2760 cm^{-1} Si-O-D band. The broad band at 3500 cm^{-1} attributed to physically adsorbed water is shifted to a band at 2620 cm^{-1}.[33] Variousauthors report that the band at 3660 cm^{-1} due to weakly hydrogen bonded silanol could not be removed completely on deuteration.[34, 27]

The major portion of the recent work on silica has been carried out to determine the following physical characteristics:

a) the number and degree of pairing of surface hydroxyl groups,

b) the mode of formation of hydroxyl groups within the bulk of the sample and

c) the degree of mobility of surface hydroxyl groups at high temperature.

Hockey and Pethica[17] have studied the dehydration and rehydration of two silica powders, Manosil and Aerosil by gravimetric, water adsorption and spectroscopic method. They assumed that the presence of both geminal and vicinal hydroxyls (Fig. 2) on the basis of a β-tridymite surface:

Fig. 2 geminal hydroxyl vicinal hydroxyl

On this type of surface (Fig. 3), each surface hydroxyl of the geminal type has a neighboring single hydroxyl in the second layer silica atom.

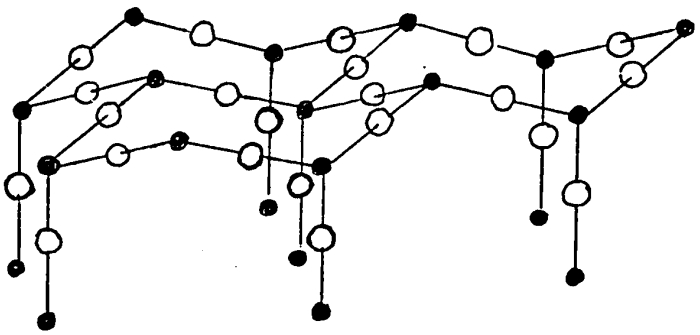
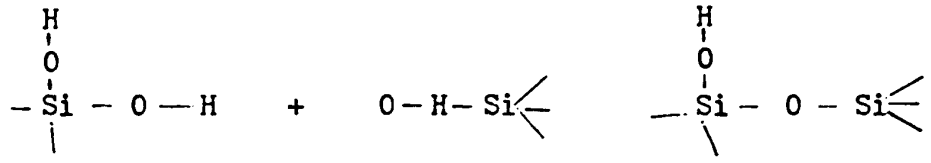
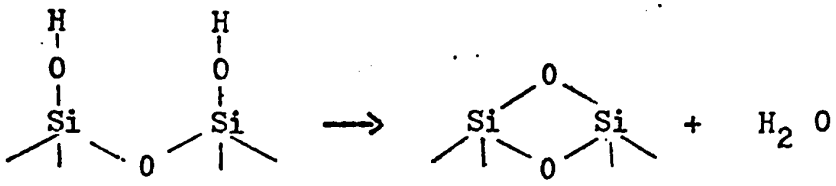


Fig. 3 The structure of β-tridymite. The open circles represent oxygen atoms and the black circles represent silicon atoms.

At low temperatures the distance between these two hydroxyls are too large to cause condensation. On mild heating the surface contracts and the hydroxyls condense to produce a strained Si-O-Si bridge and water:



The Si-O-Si link is unstable and quickly rehydrates in presence of water. At high temperatures during dehydration and contraction to Si-O-Si link becomes unstrained due to lattice rearrangements and becomes unreactive to water. Single hydroxyls dehydrate in the following manner:



On highly heated surfaces where only isolated hydroxyls are present, dehydration is possible only if either the protons or the O-H groups become mobile on the surface. Although the removal of either the hydroxyls or the protons will leave free valencies on the surface, proton loss was considered to be more probable. No proof of the mobilities of these surface groups have been presented to date.

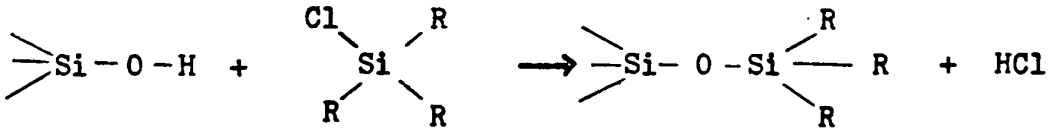
Davydov [27] and other workers [34,12,35] have suggested that hydroxyls exist within the bulk of the molecule. Hambleton and Hockey [34] have shown that hydroxyl groups exist within microporous cavities of molecular dimensions and that some of these are inaccessible to adsorbate molecules such as D_2O BCl_3 and N_2 due to steric factors. Reactions with diborane, [10] CH_3MgI, CH_3Li [35] have shown that O-H groups present on high temperature heated silica surfaces cannot also be completely removed on reacting with these adsorbents, suggesting the

presence of bulk hydroxyls that cannot be removed on heating. McDonald [13] has suggested that no hydroxyl groups remain on silica heated at higher temperatures but reform at lower temperatures by adsorbing small amounts of water.

Peri [36] has attempted to determine the number of paired hydroxyls present on dried silica gel by a detailed study of their reactions with $AlCl_3$ and $SiCl_4$. Dried silica samples, heated at various temperatures from 200 - 800°C were allowed to react with $AlCl_3$ in vacuo for a determined period of time. The outgoing gas was trapped in a NaOH solution (1 N) which was then titrated to determine the HCl produced. From this he calculated the number of paired hydroxyl groups on the surface assuming that each molecule of $AlCl_3$ reacted with either 1, 2 or 3 hydroxyl groups. The silica samples were chosen not to have any bulk hydroxyls after calcinating at 600°C. His results showed that for most types of silica, the incidence of paired hydroxyls were quite high and decreased slowly with higher drying temperatures. Drying at 400°C gave more than 95%, at 600°C 85% and about 60% at 800°C. This author concluded that after high temperature heating, the paired hydroxyls could only be geminal types which could condense only if the surface groups were mobile.

In a recent paper Hair and Hertl [37] have presented some evidence for the presence of surface geminal groups. On reacting mono and polyfunctional chloromethylsilanes on

preheated silica with only single or geminal hydroxyls, the authors assumed two types of reactions to be possible:



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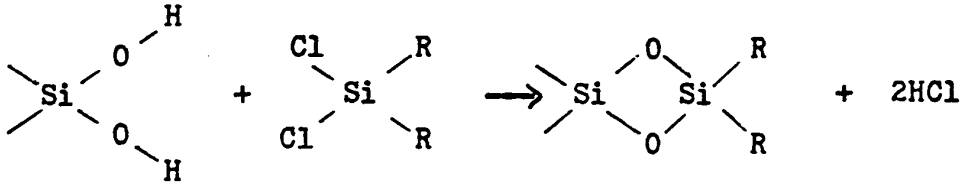


(2)

Reaction (1) involving single hydroxyls were expected to have 1.0 order kinetics and reaction (2) with geminal sites to have 2.0 order kinetics with respect to the number of surface bonding sites. The overall reaction order was found to be 1.4 suggesting the presence of almost equal ratio of single and geminal hydroxyls on the surface.

Boron Halides on Silica

Silica and alumina treated with BF_3 have been known to promote catalytic activity and selectivity in various reactions. Silica treated with BF_3 has been used in the polymerization of isobutylene[38] and in the alkylation of benzene[39]. BF_3 treated with alumina has been used to crack cumene[40] and to convert olefin-isoalkane mixtures into pure olefin.[41] Until recently very little work was done to investigate the surface reactions involved and the species produced thereby. Neimark et al[42] first found that the degree of adsorption of various organic compounds on silica decreases when the adsorbent is treated with BF_3. Chernov[43] reports that BF_3 irreversibly chemisorbed on alumina at temperatures ranging from 20 - 400°C does not change the adsorptive properties of alumina significantly.

Topchiev[44] reports that the adsorption of BF_3 on silica is reversible and that the surface species is extremely stable on heating. At 300°C 50-85% and at 400°C, 28% of the BF_3 were retained. Babuskin[45] was first to obtain a spectrum of BF_3 on alumina; two bands were produced corresponding to the asymmetric valence vibrations gas phase $B^{11}F_3$ and $B^{10}F_3$ respectively and a broad band from 1440-1250 cm^{-1} which he assigned to B-O stretching vibrations. On heating for 5 hours at 100°C, the first

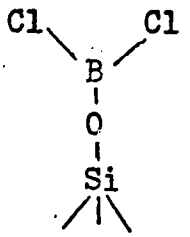
two bands disappeared and a new band at 1300 cm^{-1} appeared which was assigned to O-F stretching vibrations.

On adsorbing 0.1 mm $B^{11}F_3$ in vacuo to a 50 mg. Silica sample, Morrow[46] obtained a broad band with well resolved shoulders at 1503, 1453, 1409, 1389 and 1352 cm^{-1}. On evacuation, the 1453 and 1503 cm^{-1} bands decreased as the 1409 cm^{-1} band grew. On adding air to the sample, a broad band was always observed with two peaks at 1409 and 1380 cm^{-1}. The 1503 cm^{-1} band was $\frac{1}{4}$ the intensity of the 1453 cm^{-1} band. A poorly visible band at 685 cm^{-1} was present but disappeared when the 1503 and 1453 cm^{-1} bands did. There were no bands in the 1000 - 800 cm^{-1} region. The bands did not change on further evacuating at 100°C for 8 hours. The initial change was attributed to the small hydrolysis of the surface species.

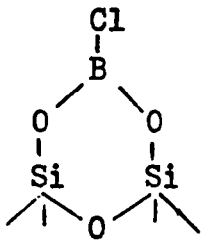
During the course of this investigation, Basilla and Rhee[47] reported the spectra of BF_3 and BCl_3 adsorbed on silica and alumina. Their results are discussed in detail in page 48.

Boron trichloride has been used as a molecular probe for gravimetric and spectroscopic investigations of the silica surface.[14,34,35,48] Hambleton and Hockey[34] reports that BCl_3 adsorbs rapidly on silica surfaces containing bulk hydroxyls although it cannot react with all the internal hydroxyls due to steric hindrance. The adsorbed

species is easily hydrolysed and on hydrolysis, produced a band at 3695 cm^{-1} which the authors assigned to O-H stretching vibrations of surface B-O-H groups. They have proposed that two possible species are produced on BCl_3 adsorption:



(a)



(b)

Armistead and Hockey[35] found that BCl_3 adsorbed on silica nonselectively with respect to single and hydrogen bonded surface groups. The authors assumed that during adsorption BCl_3 forms a transition complex with the oxygen atom. The transition from planar BCl_3 (2 sp^2) to tetrahedral (2 sp^3) configuration makes this possible. The low energy of transition facilitates the formation of the transition complex and makes BCl_3 adsorption non-selective.

The adsorption studies carried out so far suggests that both BCl_3 and BF_3 are chemisorbed on the silica surface with the possible formation of a B—O bond. Silica is transparent to infrared radiation in the 1600-1300 cm^{-1} and 1000-800 cm^{-1} regions and since most B—O stretching frequencies occur between 1500-1200 cm^{-1}

region and the BCl_3 gas phase valence vibrations [49] in the 1000-800 cm^{-1} region, it seemed worthwhile to study the infrared spectra of BF_3 and BCl_3 adsorbed on silica. Further, the evidence presented to date has shown that various types of hydroxyl groups exist on the silica surface depending on the temperature of dehydration. Since the chemisorption of BF_3 and BCl_3 possibly involves the interactions with these hydroxyls, the infrared spectroscopic studies with silica samples heated at various temperatures will not only give information on the surface reactions but may also provide some insight into the nature of the surface hydroxyls present.

EXPERIMENTAL

Materials

Silica: The silica used in this laboratory was Cab-O-Sil, grade M-5, obtained from the Cabot Inc. of Boston, Mass., U.S.A. It is prepared by the flame hydrolysis of silicon tetrachloride at 1000°C

$$SiCl_4 + 2H_2 + O_2 \longrightarrow 4\,HCl + SiO_2$$

The oxide has a surface area of 150-200 m^2/g and particle size of 120Å. Both normal boron trifluoride and boron trichloride were obtained from Matheson Limited of Whitby, Ontario, Canada and contained the natural B^{11} and B^{10} isotope ratio of 4:1.

$B^{10}F_3$: This compound was prepared in this laboratory by the following method: a known amount of CaF_2. $B^{10}F_3$ obtained from Oak-ridge National Laboratories at Oak-Ridge, Tenn., U.S.A. was heated in vacuo with an electrical heating device that maintained the temperature at 250°C; gaseous $B^{10}F_3$ thus released was collected into another flask cooled with liquid nitrogen.

$B^{10}Cl_3$: This was prepared in the laboratory by the following method:[50] aluminum chloride was heated in vacuo over an open flame and was allowed to react with $B^{10}F_3$ admitted into the reacting vessel through an inlet tube. The product $B^{10}Cl_3$ was distilled off while the aluminum fluoride

(AlF_3) peeled off from the walls of the flask as a light powder The $B^{10}Cl_3$ was then cooled and collected in a tube maintained at -80°C with a dry ice-acetone mixture.

Sample preparation: Fifty mg. samples of Cab-O-Sil, pre-heated in a furnace at 600°C in order to oxidize any organic contaminants, were pressed into self supporting pellets in a 25 mm. diameter steel die similar to those used for making KBr pellets. Pressures of the order of 20,000 lb cm^2 have been reported to be necessary, but pressures from 1,000-2,000 lb in^2 applied for few seconds sufficed to give pellets of good infrared transparency. Because the silica discs expanded and cracked against the wall of the die when the pressure was released, a small wound strip of glass wool was placed as a cushion inside the die before adding the oxide.

Experimental: The Pyrex vacuum line used for heating, and evacuating the sample is shown in Figure 4. The high vacuum stopcocks were lubricated with Apiezon "N" grease. A mercury manometer was used to measure pressures greater than 1 Torr. and a thermocouple vacuum gauge (Consolidated Vacuum Corporation of Rochester, New York, U.S.A.) was used to measure pressures from $1\text{-}10^{-3}$ Torr. The vacuum was maintained by a mercury diffusion pump and a mechanical oil pump; the line was separated from these by two liquid nitrogen traps. The cell containing the samples was joined to the vacuum line

via a ball joint system so that it could be placed either horizontally or vertically as required. Two bulbs of varying capacities were calibrated. From these a measured amount of gas could be expanded to give various known pressures of gas.

The cell used has three detachable parts which were assembled in the manner shown in Figure 5. Part A is a 30 cm. long, 1.5 cm. in diameter pyrex tubing attached to a broader base with a socket and a stopcock leading to the vacuum line. Part B is a 2.5 cm. diameter 29 cm. long quartz tube (a smaller pyrex tube was used for experiments done at temperatures lower than 500°C) and could be heated up to 1040°C. Five and half feet of nichrome heating wire were wound externally around the quartz tube and this was insulated by a thick coating of powedered asbestos. Thermocouple (chromel-alumel) wires were so placed to record the temperature of the heated external surface of the quartz tube. Part C was a pyrex cell with a six inch base and a socket. Two highly polished NaCl windows of 5.5 cm. diameter and 5 mm. thickness were sealed with Glyptal G to the cell. Inside the cell base two small glass notches were placed to position the sample holder.

The platinum sample holder was attached to a 40 cm. long steel tubing and had a 2.5 X 1 cm. rectangular slot into which the pellets were mounted. Inside the other end of the tube a small magnet was inserted so that the holder,

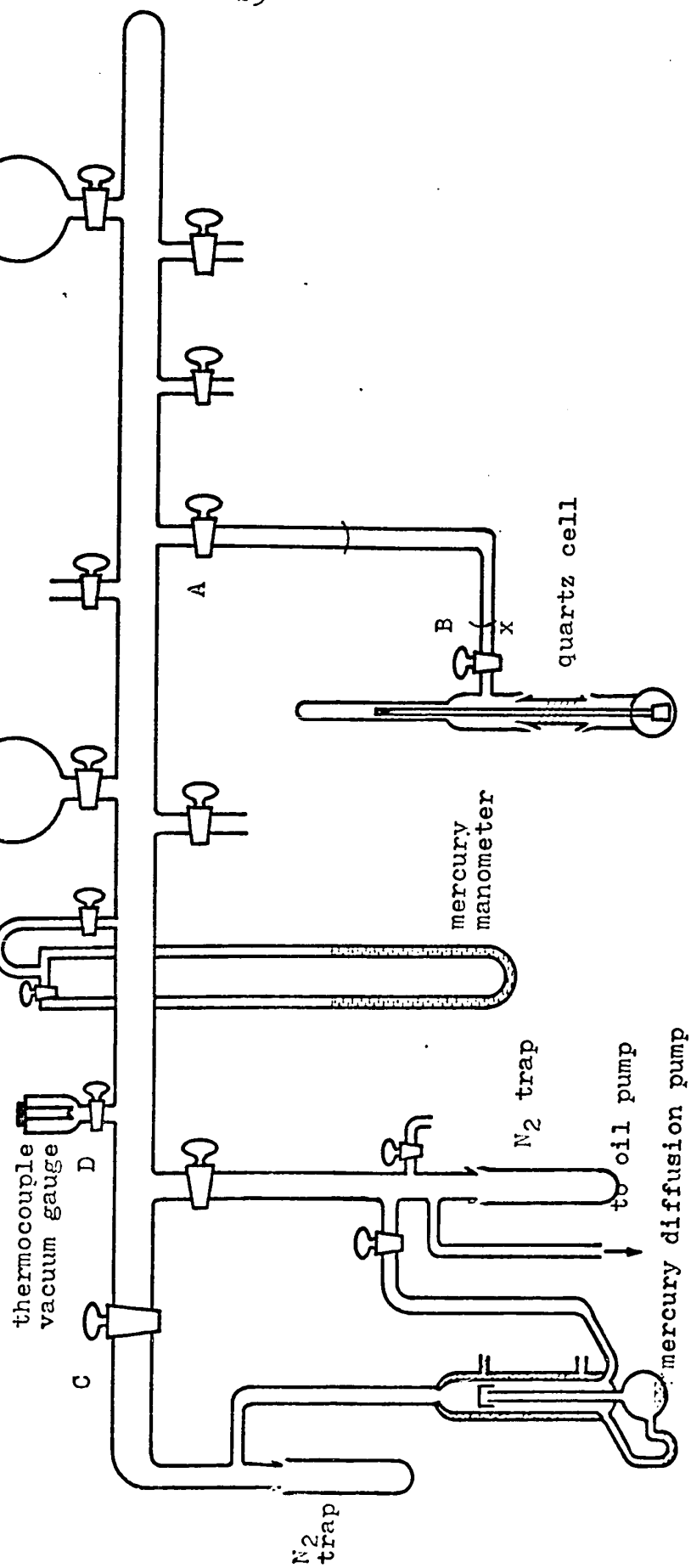
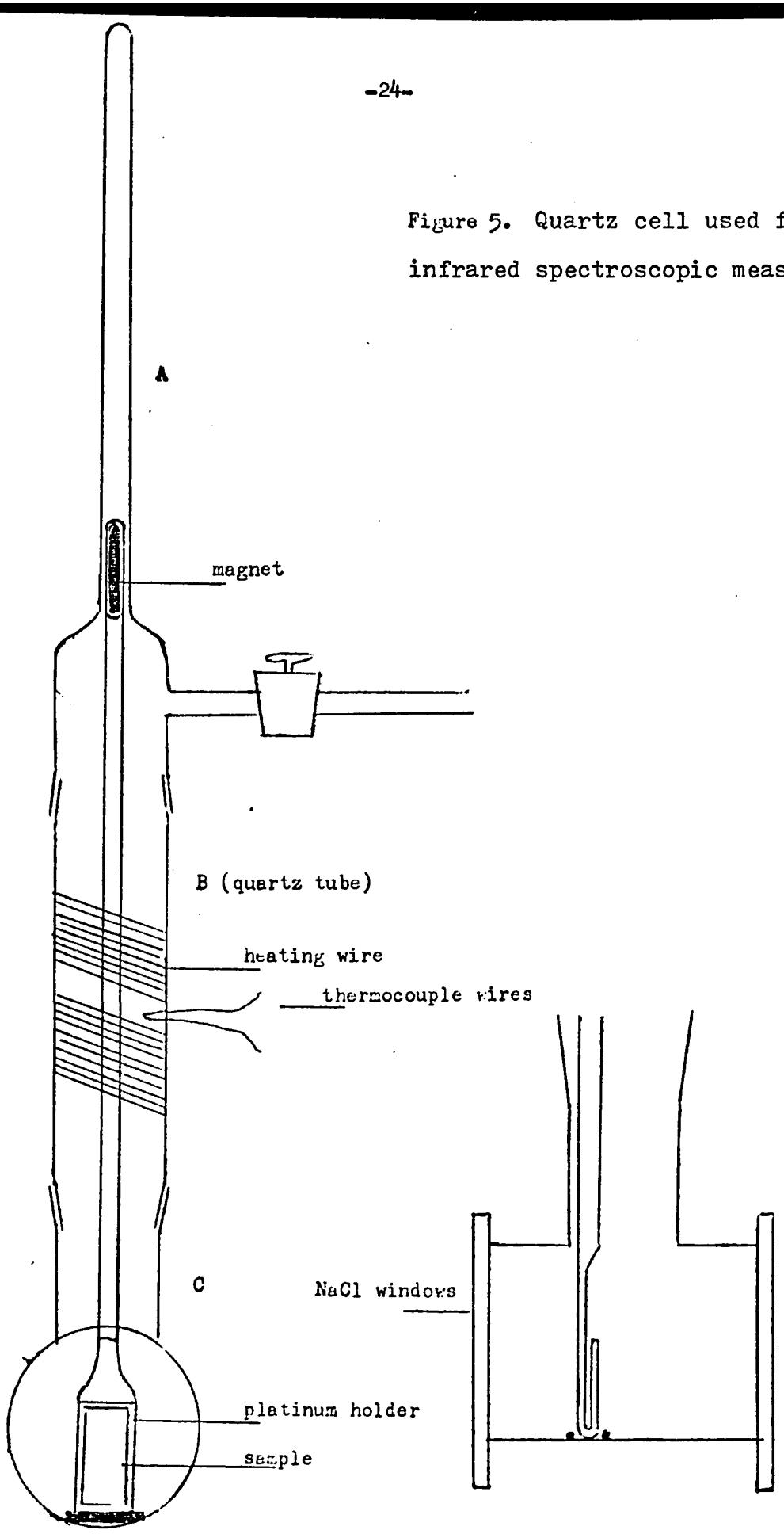


Figure 4. Vacuum line used for sample preparation.

Figure 5. Quartz cell used for infrared spectroscopic measurements



when placed inside the cell, could be manipulated easily by an external magnet. The steel at the platinum - steel joint which was exposed to the highest temperature region disintegrated and had to be rewelded periodically using spot-welding techniques.

The cell was placed horizontally when heated and it was possible to slide the holder down in order to position the sample at the center of the heated region. Temperatures at the joints were maintained below 30°C by blowing air from mechanical blowers situated under each joint. After heating, the cell was allowed to cool down to room temperatures. The holder was then carefully placed between the two glass notches at the base of the cell. To prevent the pellets from sliding out, all other operations were carried out with the cell at a vertical position Apiezon 'H' grease was used at the cell joints.

The general experimental procedure was as follows: after heating, the sample was cooled to room temperature. The cell was detached from the vacuum line (fig. 4) and the background spectra of the sample was recorded. The sample was then reclamped to the vacuum system at x and stopcock A was opened. After 30 minutes evacuation, the stopcock B was opened to expose the sample to the vacuum system. Stopcock C was then closed to cut off the pumping arrangement and the required amount of gas was admitted to the cell. Boron halides are extremely reactive to silica

and only small amounts, to the order of 0.01-2 cm., were reacted for 10-15 seconds at room temperatures. Because boron halides corrode the filament in the vacuum gauge, stopcock D was left closed at all times when the gases were being admitted to the vacuum line. The excess gas was then pumped off by opening stopcock C and the cell was evacuated for few seconds and its spectra recorded. The infrared spectra were obtained with a Perkin-Elmer model 13-G filter grating spectrometer. Although all spectra were taken at room temperature to obtain comparable band intensities, it is known [2] that the heating effect of the source light does increase the temperature of the sample up to 20°C.

RESULTS

BF_3 Adsorbed on Silica

The background spectrum of a silica sample in the 4000-600 cm^{-1} region is shown in figure 6. From 3750-3300 cm^{-1} the bands due to surface silanol groups are present and from about 3300-2130 silica is very transparent to infrared radiation. At about 2130 cm^{-1} the overtone and combination bands of silica begin to appear and the transmission decreases producing a slanting background spectrum. Silica absorbs totally in the 1280-980 cm^{-1} region. The 980-845 cm^{-1} region (Fig. 6b) is transparent to infrared with a maximum 50% transparency at 920 cm^{-1}. The 845-780 cm^{-1} region is again opaque to infrared radiation and the region from 780-650 exhibits an approximately 35% transmission.

The background infrared spectra in the region of 4000-3000 cm^{-1} of 50 mg. silica discs evacuated at various temperatures in the range of 400-1020°C are shown in figure 7. On evacuating a silica sample at 400°C an intense sharp band at 3749 cm^{-1} attributable to the O-H stretching vibrations of Si-O-H groups is present (Fig. 7a) and there are no bands in the 1000-800 cm^{-1} region. The intensity of the 3749 cm^{-1} band decreases as the dehydration temperature of the silica sample is increased. The 3749 cm^{-1} band of a silica sample evacuated at 900°C is about 40% the intensity (Fig. 7b) of the same band in figure 7a. In the spectrum of a silica sample evacuated at 800°C, there is a pair of weak bands at 908 and 890 cm^{-1} (Fig. 8a). The intensities

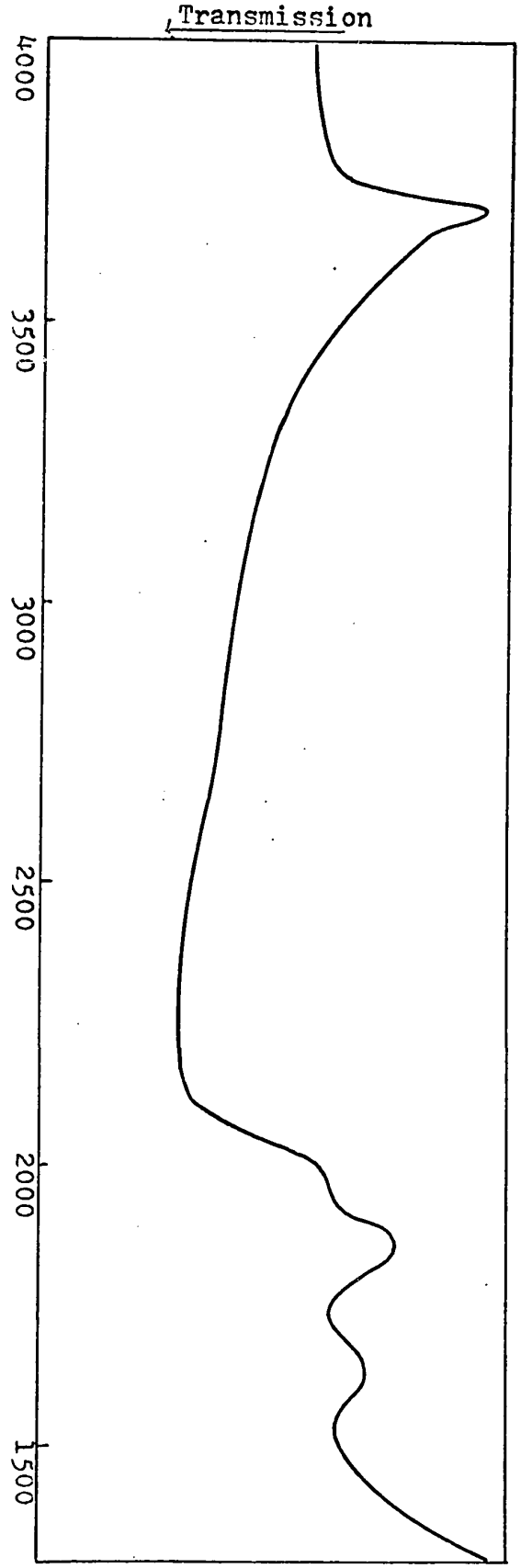


Fig. 6-a Silica background spectrum

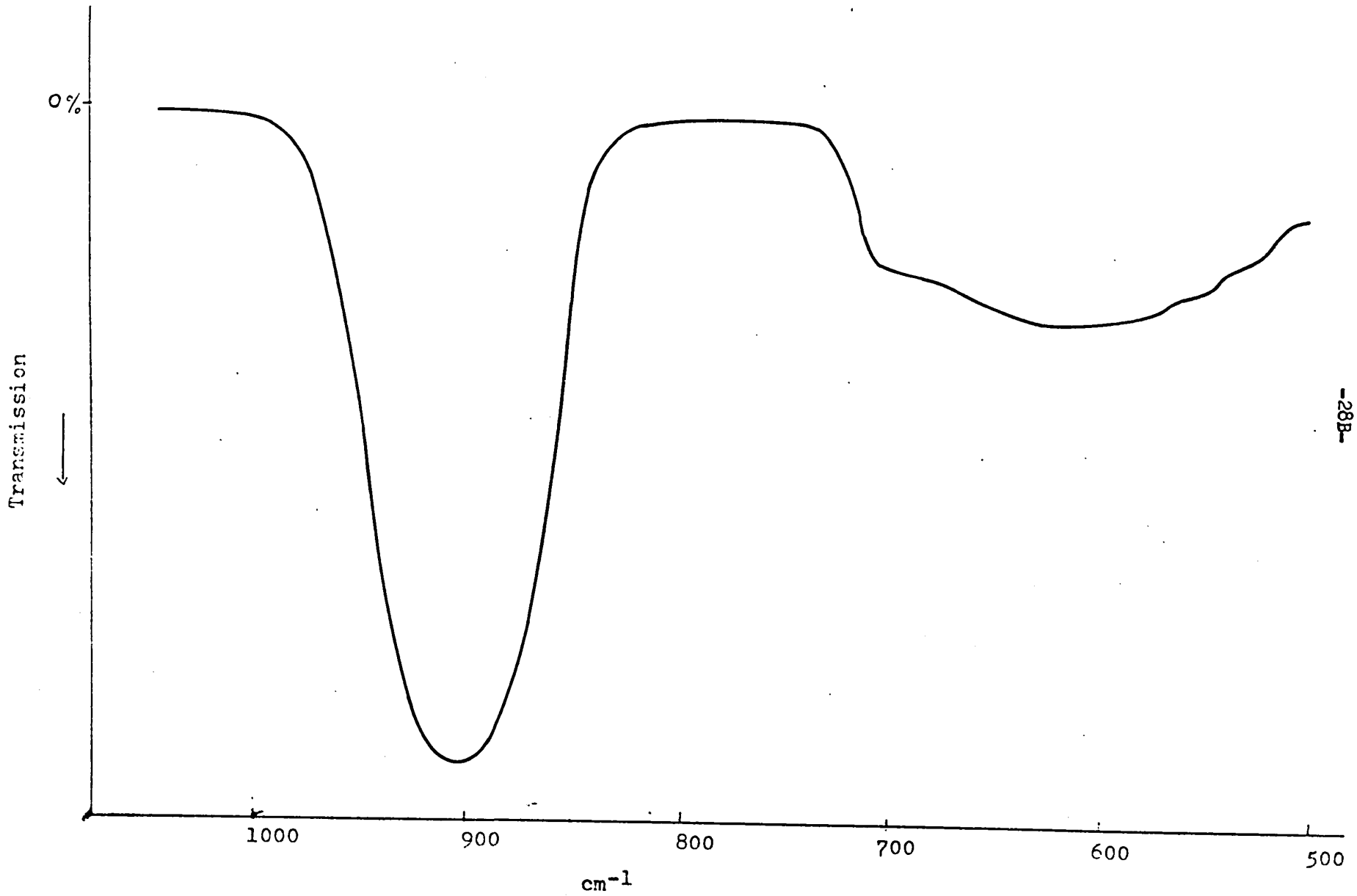


Fig. 6-b Silica background spectrum

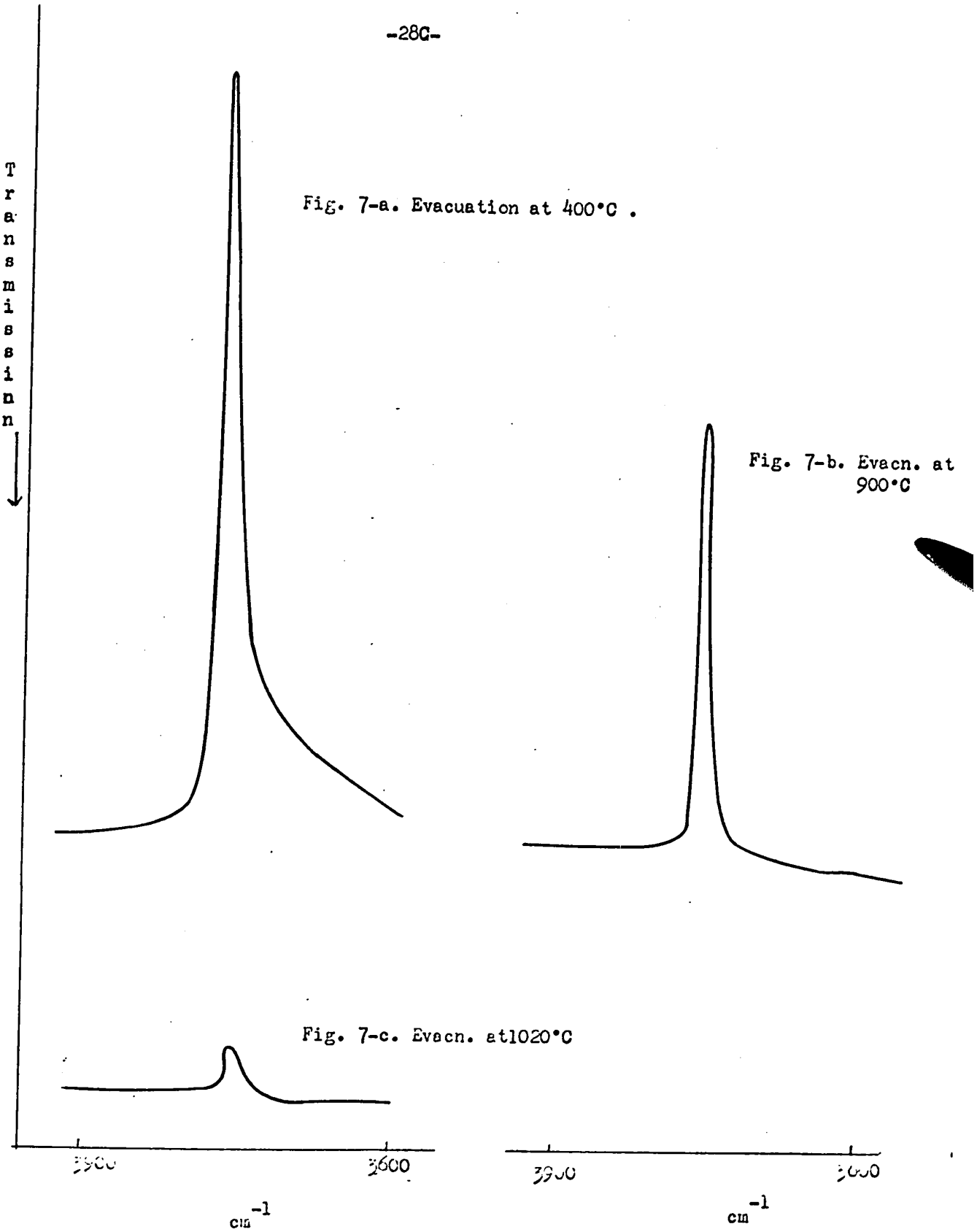


Fig. 7-a. Evacuation at 400°C .

Fig. 7-b. Evacn. at 900°C

Fig. 7-c. Evacn. at1020°C

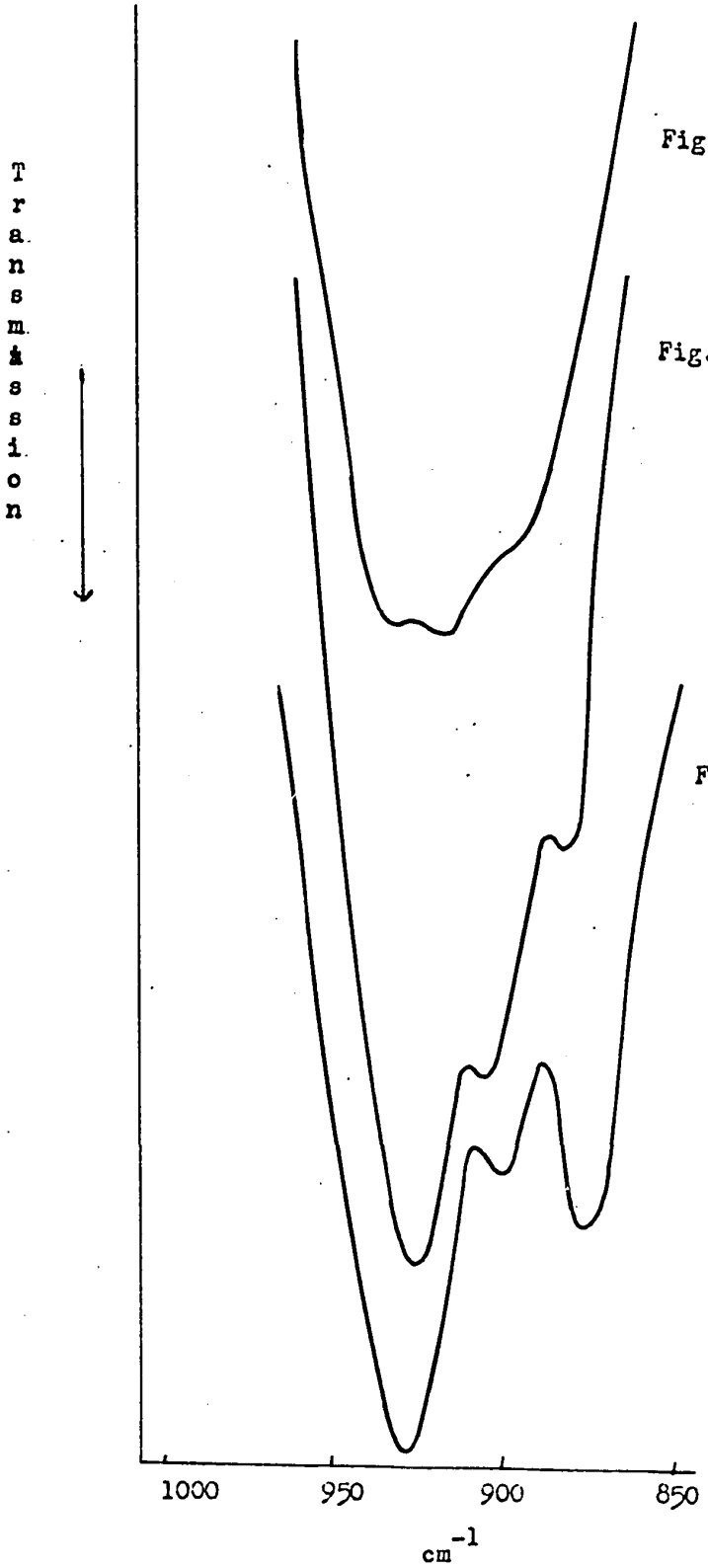


Fig. 8-a. Evac. at 800°C.

Fig. 8-b. Evac. at 900°C.

Fig. 8-c. Evac. at 1020°C.

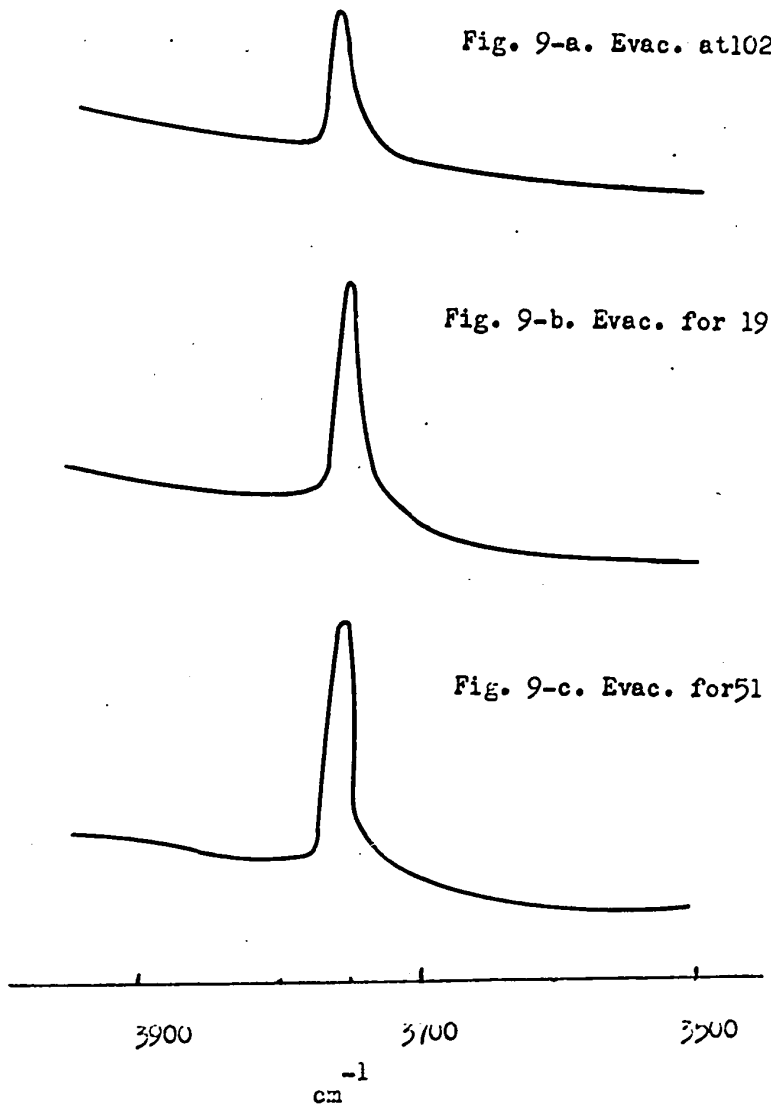


Fig. 9-a. Evac. at1020°C.

Fig. 9-b. Evac. for 19 hours.

Fig. 9-c. Evac. for51 hours.

of these bands increase as the intensity of the 3749 cm^{-1} band decreases with higher temperatures of evacuation. The 3749 cm^{-1} band is almost removed in the spectrum of a silica ~~sample~~ sample evacuated at 1020°C (Fig. 7c) and the two bands at 908 and 890 cm^{-1} are now very intense (Fig. 8b). Silica samples evacuated at temperatures below 400°C exhibit an additional broad band at 3230 cm^{-1} due to physically adsorbed water which can be removed on heating at 400°C.

The spectrum of a silica sample evacuated at 1020 for 7 hours (Fig. 9a) exhibits a band at 3749 cm^{-1} of 0.05 O.D. (optical density). It is seen that on evacuating this sample at room temperature for 19 hours, the band intensity has increased to O.D. 0.08 (Fig. 9b) and after 51 hours evacuation to O.D. 0.10 (Fig. 9c).

Figure 10a shows the spectrum in the 1650-1300 cm^{-1} region of a silica sample to which 0.2 cm of B^nF_3 had been admitted at room temperature for 10 minutes followed by evacuation for 2 minutes. Prior to adsorption the sample was heated in vacuo at 900°C for 6 hours. There are three strong bands at 1500, 1452 and 1393 cm^{-1} (set I_a) of O.D. 0.34, 1.2 and 0.56 respectively and a shoulder at 1409 cm^{-1} (Fig. 10a). Figures 10b-e show the spectra of the same sample after 4, 20, 44 and 97 hours evacuation subsequent to B^nF_3 adsorption. After 4 hours evacuation, an additional band at 1341 cm^{-1} is present. The I_a bands have decreased and the 1409 cm^{-1} band has increased in intensity (Fig. 10b).

On further evacuation, the set I_a bands gradually decrease as both the 1409 and 1341 cm^{-1} (Set II_a) bands continue to grow. After 44 hours evacuation, the 1500 and 1452 cm^{-1} bands have decreased to 30% of their initial band intensities. The 1409 and 1341 cm^{-1} (Set II_a) bands have become more pronounced and the 1393 cm^{-1} band is present as a weak shoulder (Fig. 10-d). After 97 hours evacuation (Fig. 10-e) the intensities of the set I_a bands have greatly decreased whereas the 1409 and 1341 cm^{-1} (Set II_a) band intensities have increased. On adding air to the same sample, after 97 hours evacuation, the set I_a and set II_a bands are replaced by two bands at 1425 and 1378 cm^{-1} and a weaker band at 1475 cm^{-1} (Set III_a) (Fig. 10f). On exposing the sample to air for 24 hours the set III_a bands remain unchanged and no additional bands appear in the 1650-1300 cm^{-1} region.

The spectral changes in the 3800-3600 cm^{-1} region of the same silica sample after adding B^nF_3 are shown in figures 11a-f. On adding 0.2 cm B^nF_3 to the sample, the strong 3749 cm^{-1} band is almost totally removed (Fig. 11-b). On evacuating the disc for 4 hours, following B^nF_3 adsorption, the 3749 cm^{-1} band is almost regenerated to O.D. 0.01 (Fig. 11-c) and it continues to grow on further evacuation. The growth of this band at various stages of evacuation is shown in figures 11c-e. The increase in intensity of the regenerated 3749 cm^{-1} band parallels the growth of the set II_a bands

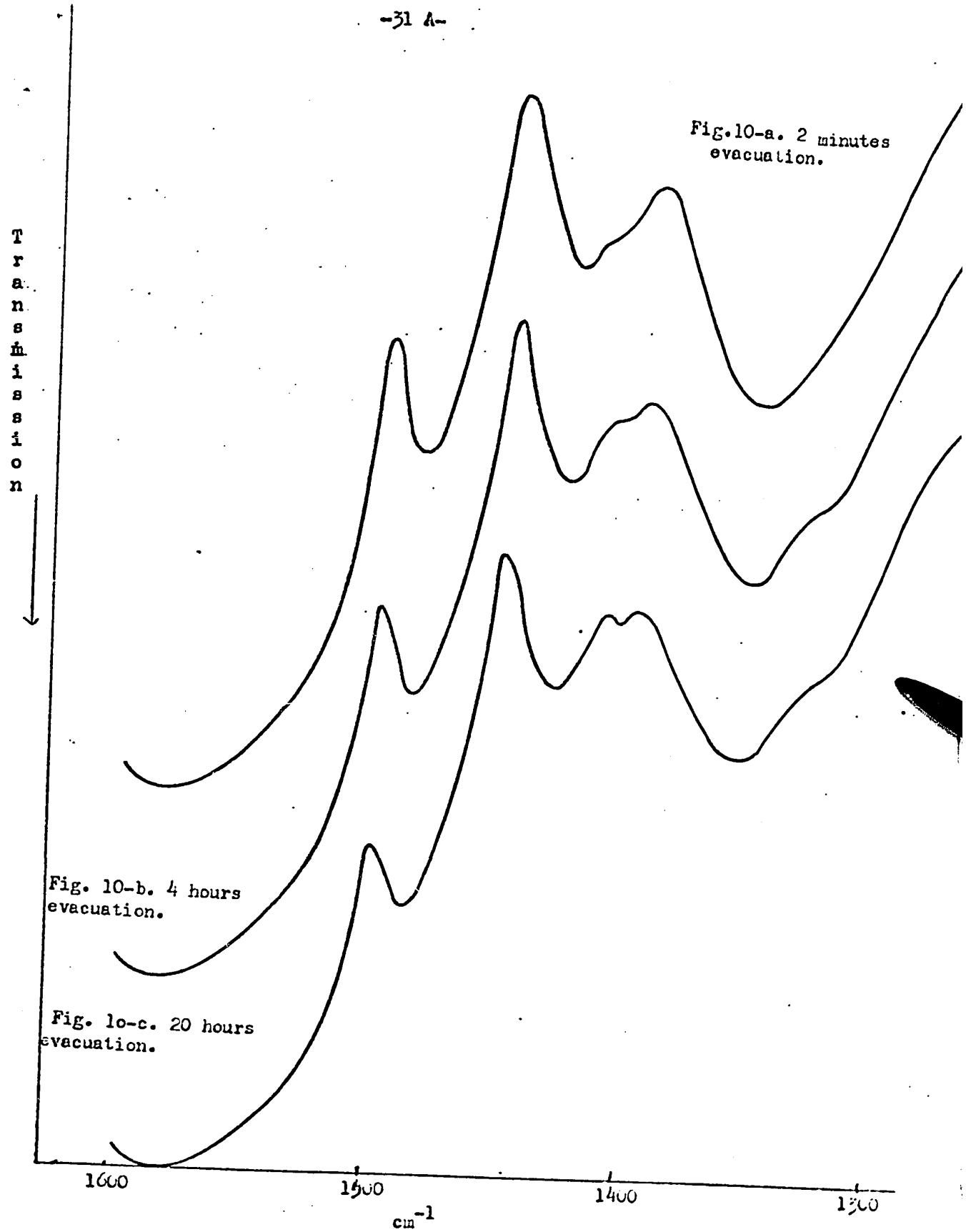


Figure 10. 0.2 cm. BF_3 adsorbed on silica.

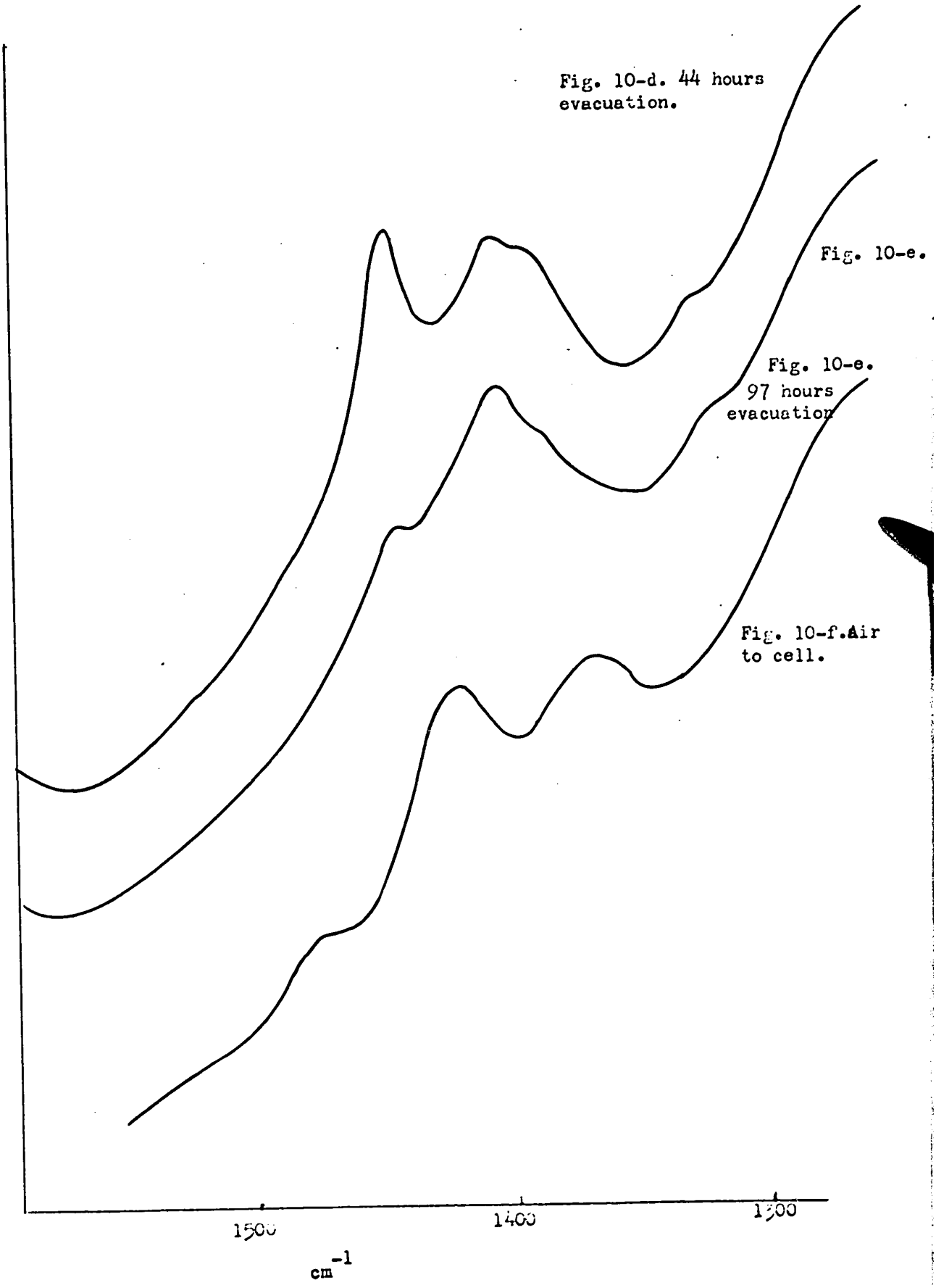


Fig. 10-d. 44 hours evacuation.
Fig. 10-e.
Fig. 10-e. 97 hours evacuation
Fig. 10-f. Air to cell.
1500
1400
1300
cm-1

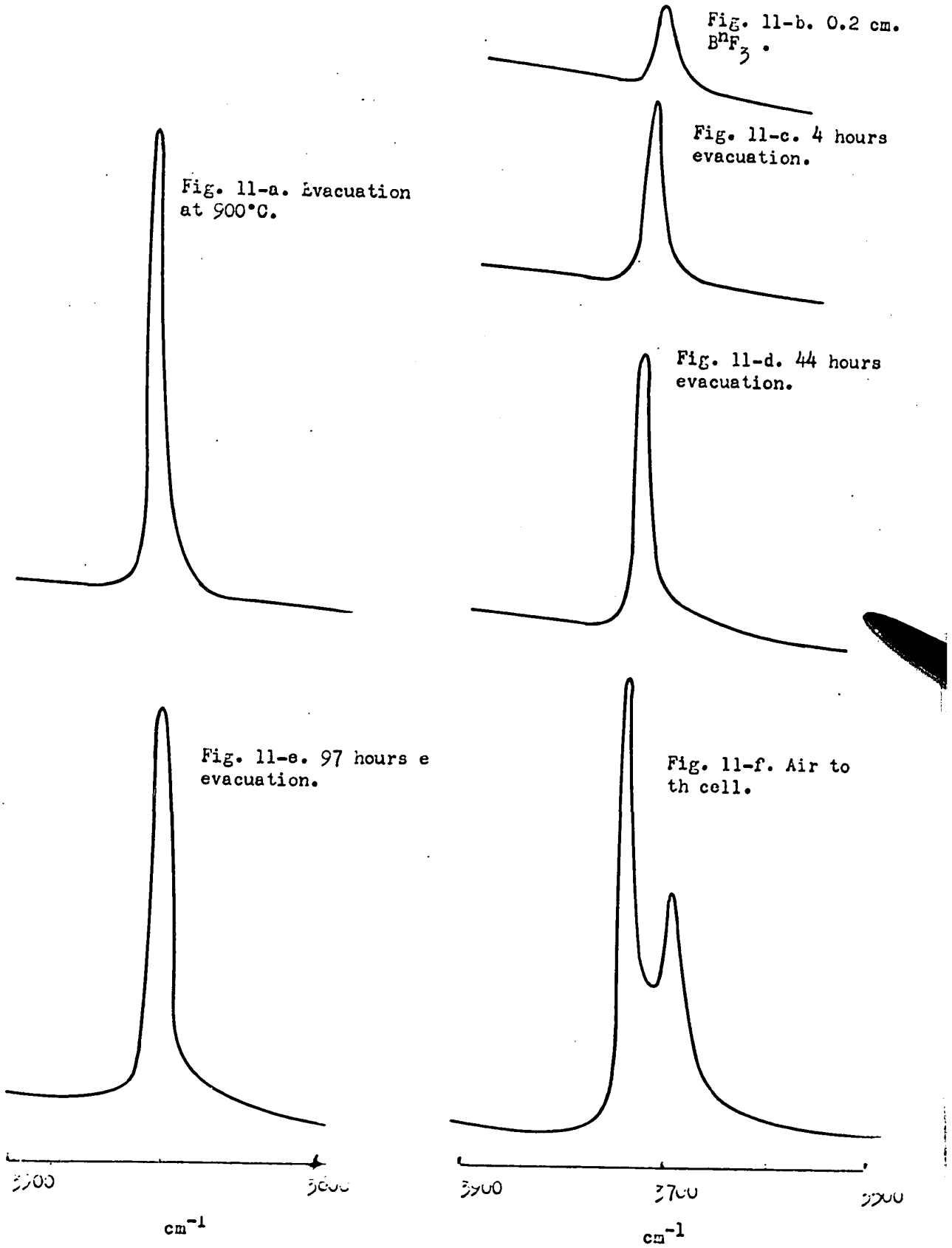


Figure 11. 0.2 cm. B^nF_3 adsorbed on silica.

and the decrease in set I_a band intensities. After 97 hours evacuation, the 3749 cm^{-1} band intensity has regained 85% of its initial value (Fig. 11e) and does not grow on further evacuation. On adding air to the sample, the intensity of the 3749 cm^{-1} band increases to its initial value and there is a less intense band at 3700 cm^{-1} (Fig. 11-f).

$B^{10}F_3$: Figures 12-a shows the spectrum of a silica sample to which 0.2 cm $B^{10}F_3$ was added for 10 sec. followed by 5 mins. evacuation. The silica sample was evacuated at 910°C for 6 hours prior to $B^{10}F_3$ adsorption. There are two strong bands at 1500 and 1448 cm^{-1} together with a shoulder at 1387 cm^{-1}. The spectra of the same sample evacuated for 2, 44 and 120 hours after $B^{10}F_3$ adsorption are given in figures 12b-d. On evacuating the same sample, the 1500 and 1448 cm^{-1} (Set I_b) bands decrease in intensity as the 1465 and 1387 cm^{-1} (Set II_b) band intensities continue to grow. After 120 hours evacuation (Fig. 12-d) a strong sharp band at 1465 cm^{-1} and the band at 1387 cm^{-1} are present. The 1500 cm^{-1} band intensity has decreased by approximately 80% from its initial value and the 1448 cm^{-1} band has diminished to a weak shoulder. The total percentage decrease of the band at 1448 cm^{-1} from its initial value could not be determined as it overlapped considerably with the adjacent 1465 cm^{-1} band. On adding air to the cell after 120 hours evacuation, the set I_b and set II_b bands are replaced by two bands at 1475 and 1420 cm^{-1} (set III_b) (Fig. 12-e). The set III_b bands remain

unchanged and no additional bands appear in the 1650-1300 cm^{-1} and 1000-150 cm^{-1} regions on exposing the sample to air for 24 hours.

The spectral changes in the 3700-3400 cm^{-1} region of the $B^{10}F_3$ treated silica sample are shown in figures 14a-c. On adding 0.2 cm $B^{10}F_3$ to the silica disc, the strong 3749 cm^{-1} band present in the background spectrum (Fig. 13a) first disappears (Fig. 13b) and then reappears after 2 hours evacuation and continues to grow on further evacuation (Fig. 13c-e). The growth of this band parallels the decrease in intensity of the set I_b bands and the growth of the set II_b bands. After 120 hours evacuation of the same sample, the 3749 cm^{-1} band intensity regained almost 80% of its initial value (Fig. 13-e). On adding air to the sample after evacuation, the 3749 cm^{-1} band becomes almost as intense as the initial 3749 cm^{-1} band present in the background spectrum (Fig. 13a) and an additional less intense band is produced at 3700 cm^{-1} (Fig. 13f). On exposing the silica sample to air for 24 hours, both the 3749 cm^{-1} and the 3700 cm^{-1} band intensities have diminished slightly and a new broad band at 3230 cm^{-1} has appeared . It is seen from figures 11 and 13 that the spectral behaviour of the bands in the 3800-3200 cm^{-1} region are similar for silica samples preheated in vacuo at 900°C to which either B^nF_3 or $B^{10}F_3$ has been added.

The 908 and 890 cm^{-1} bands present in the background spectra (fig. 14a) are removed on adding either B^nF_3 or $B^{10}F_3$ and are not regenerated on subsequent evacuation On adding air to the BF_3 treated samples a band at 880 cm^{-1} is produced (Fig. 14b).

On adding small amounts of either $B^{10}F_3$ or B^nF_3 to silica it was found that the rate of change of the set I_a (B^nF_3) and set I_b ($B^{10}F_3$) bands was faster than when larger pressures were added. Further, the same set of bands, ie sets I_a and II_a and sets I_b and II_b were produced on adding B^nF_3 and $B^{10}F_3$ respectively to various silica samples which had been evacuated at temperatures ranging from 250-940°C prior to adsorption.

The frequencies of the bands produced on adsorbing B^nF_3 and $B^{10}F_3$ to silica and the number of their corresponding sets are listed below in Table 1.

Table 1

Adsorbate	Set No	Frequencies (cm^{-1})
B^nF_3	I_a	1500, 1452, 1393
B^nF_3	II_a	1409, 1341
B^nF_3	III_a	1475, 1425, 1375
$B^{10}F_3$	I_b	1500, 1448
$B^{10}F_3$	II_b	1465, 1387
$B^{10}F_3$	III_b	1475, 1420

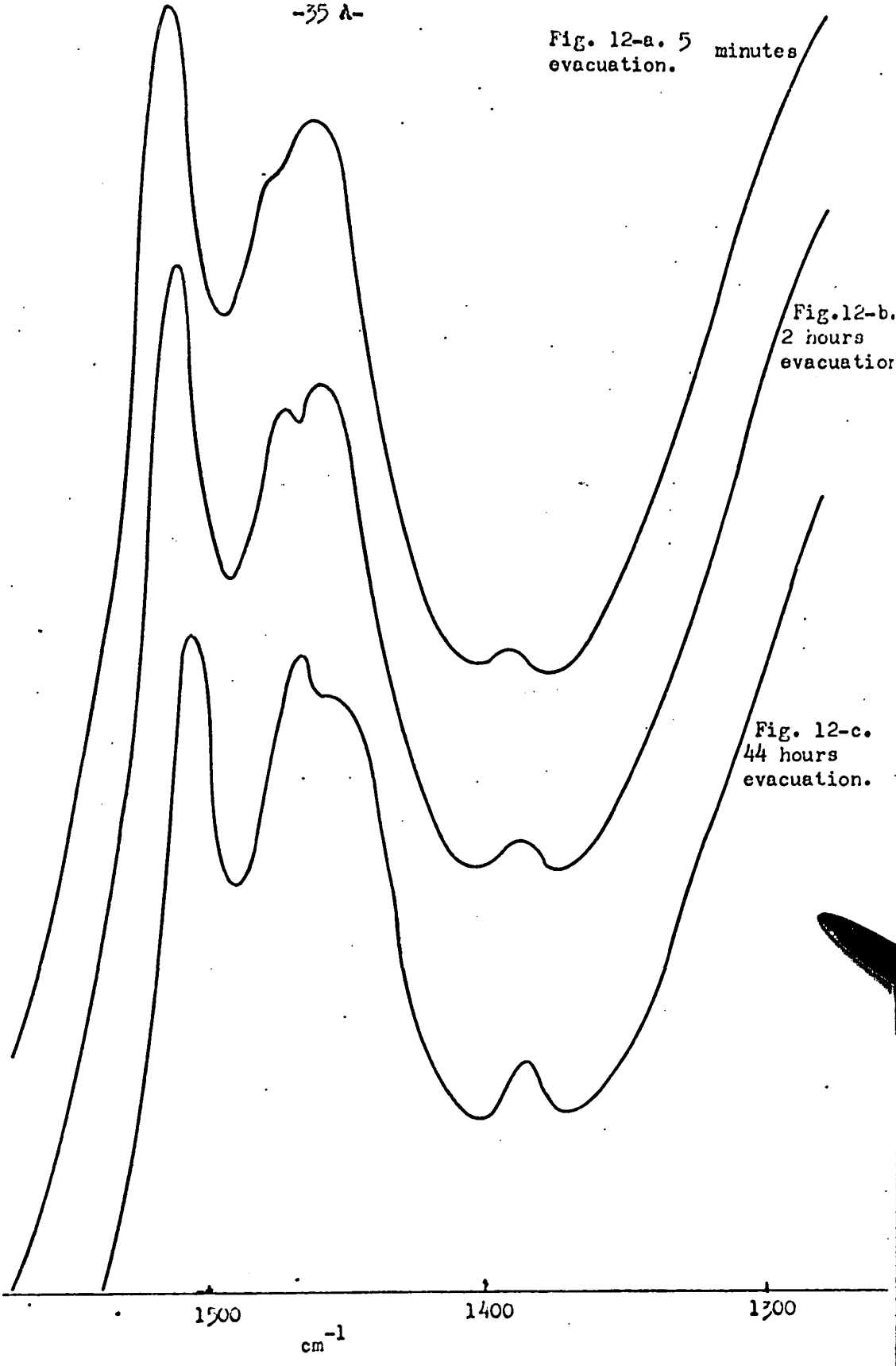


Figure 12. 0.2 cm. $B^{10}F_3$ adsorbed on silica

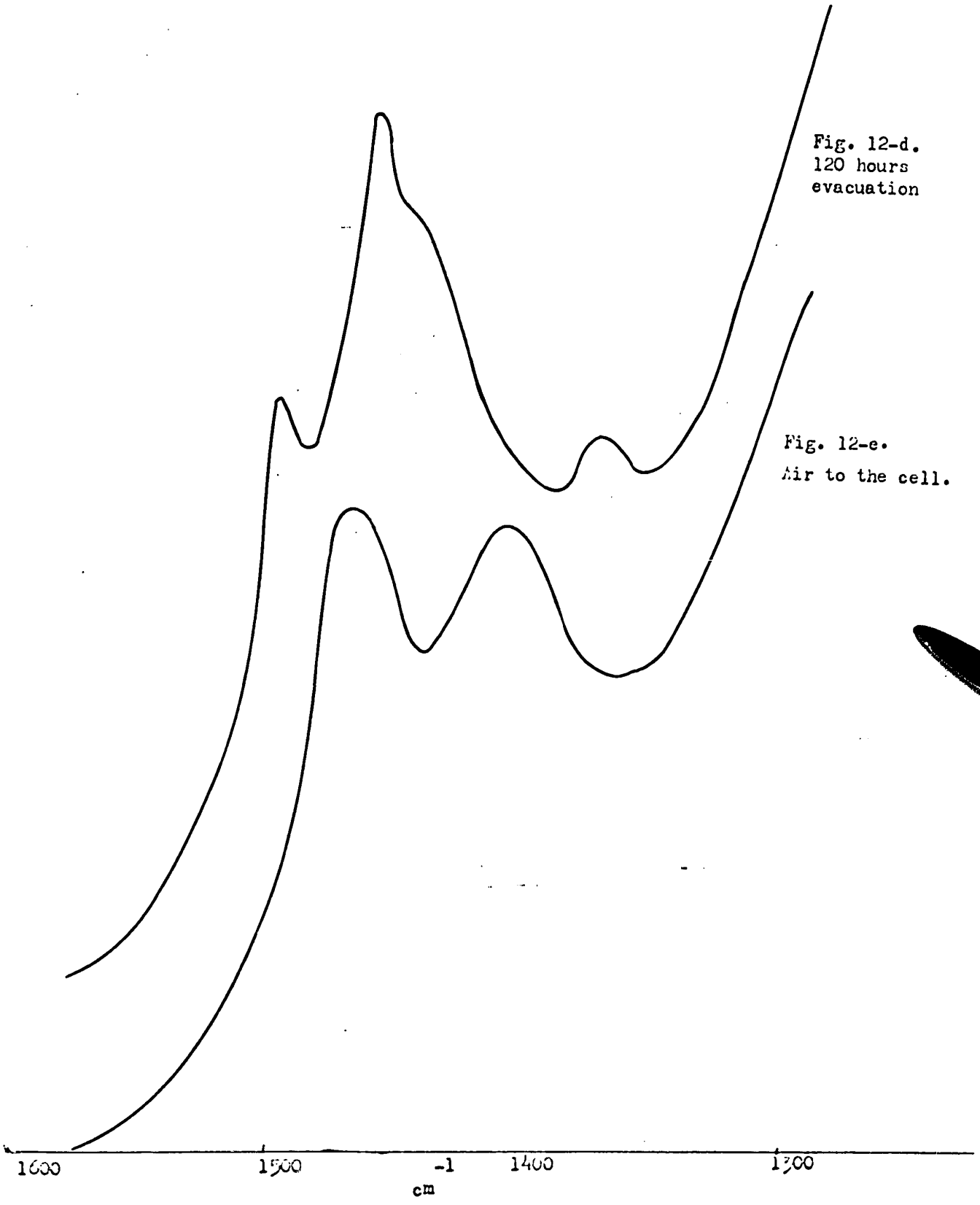


Fig. 12-d.
120 hours
evacuation

Fig. 12-e.
Air to the cell.

Fig. 13-a. Evacuation at 910°C.

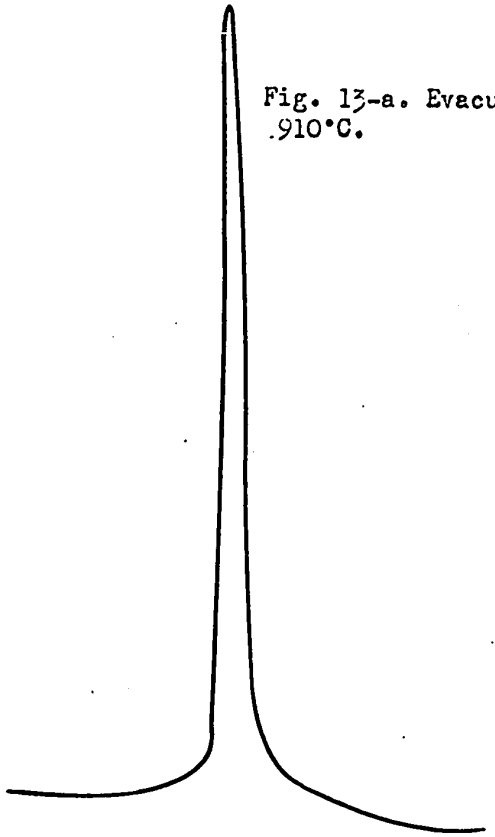


Fig. 13-b. 0.2cm. $B^{10}F_3$.

Fig. 13-c. 2 hours evacuation.

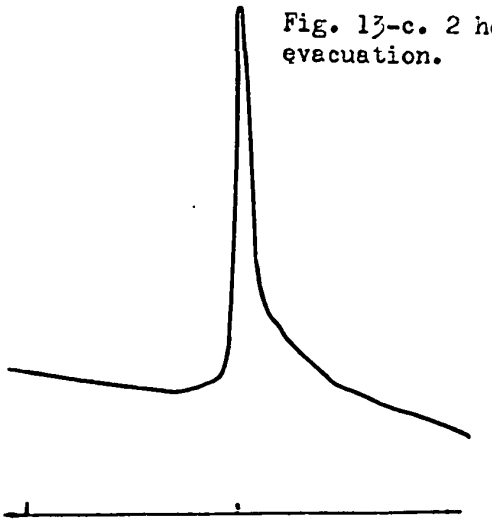


Fig. 13-d. 44 hours evacuation.

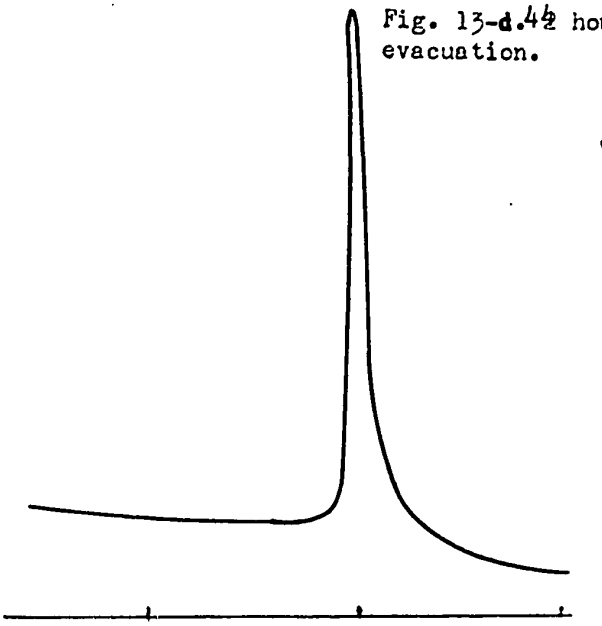


Figure 13. 0.2 cm. $B^{10}F_3$ adsorbed on silica.

Fig. 13-e. 120 hours evacuation.

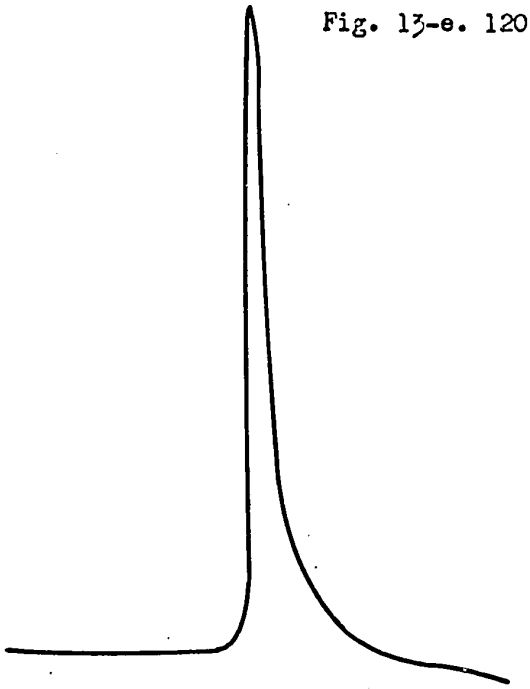
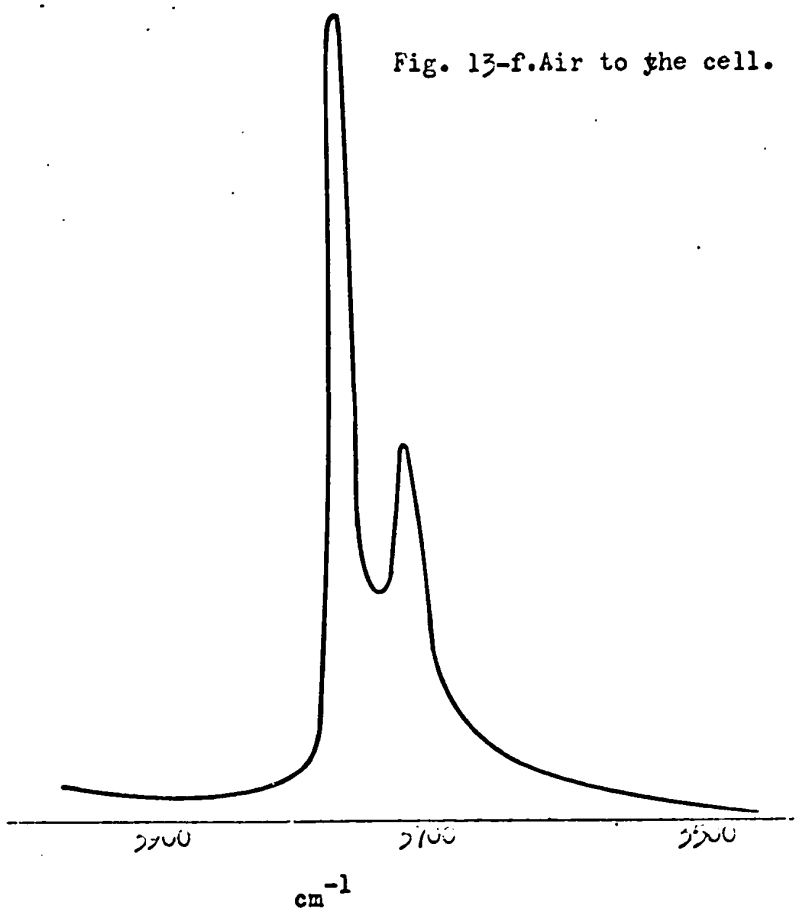


Fig. 13-f. Air to the cell.



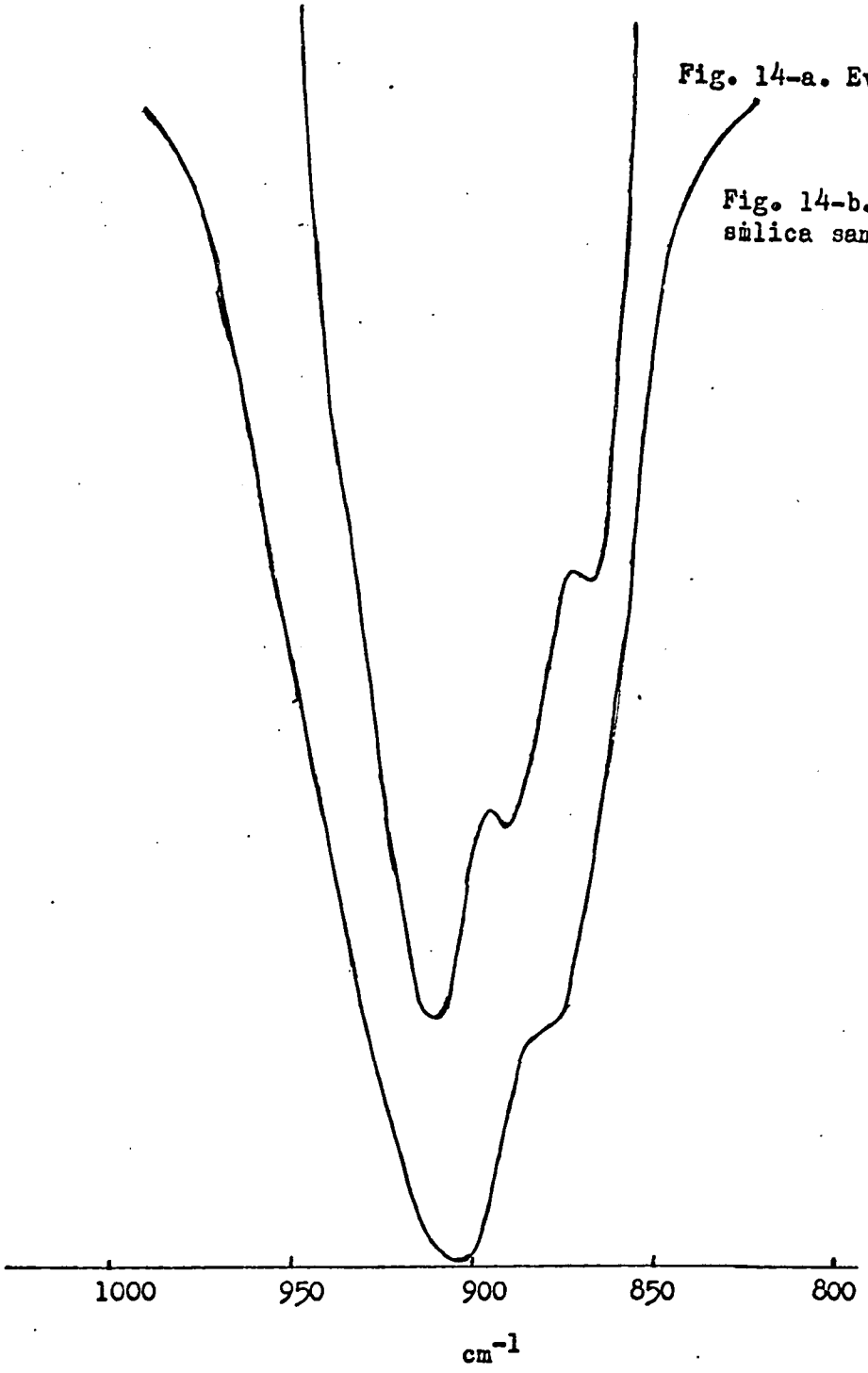


Fig. 14-a. Evacuation at 910°C

Fig. 14-b. Air to a BF_3 treated silica sample.

BF_3 On Samples Preheated at 1020°C

The background spectrum in the 3800-3400 cm^{-1} region of a silica sample evacuated at 1020°C is shown in figure 15a. The 3749 cm^{-1} Si-O-H band is almost removed and a pair of strong bands at 908 and 890 cm^{-1} are present (Fig. 16a). Figures 17a and 17b show the spectra of a silica sample to which 0.1 mm $B^{10}F_3$ was added for 15 sec. followed by 5 mins. evacuation. The silica sample was heated in vacuo at 1020°C for 10 hours prior to adsorption. Initially two bands at 1500 and 1448 cm^{-1} (Set I_b) are present (Fig. 17a). After 67 hours evacuation, the set I_b band intensities have decreased slightly and very weak shoulders at 1465 and 1387 cm^{-1} are present (Set II_b) (Fig. 17b). The 908 and 890 cm^{-1} bands are removed after adding $B^{10}F_3$ and no bands were observed in the 1000-800 cm^{-1} region on subsequent evacuation (Fig. 16b). On adding air to the cell a band at 880 cm^{-1} is produced (Fig. 16-c) and the set I_b and the weak set II_b bands are replaced by two bands at 1475 and 1420 cm^{-1} (Set III_b) (Fig. 17c).

Figures 15a-e show the spectra in the 3800-3100 cm^{-1} region of the same sample to which $B^{10}F_3$ has been added. The intensity of the very weak 3749 cm^{-1} band present in the background spectrum (Fig. 15a) does not change on adding $B^{10}F_3$ and increases slightly on subsequent evacuation (Figs. 15b-c). On adding air to the sample after 110 hours evacuation, the 3749 cm^{-1} band intensity increased to O.D. 0.17

and a less intense band at 3700 cm^{-1} of 0.09 O.D. was present (Fig. 15d). After exposing the sample to air for 24 hours the 3749 cm^{-1} and 3700 cm^{-1} bands have increased to O.D. 0.21 and 0.13 but there were no additional bands in this region (Fig. 15e).

Fig. 15-a. Evacuation at 1020°C.

Fig. 15-b. 0.1 mm. $B^{10}F_3$.

Fig. 15-c. 110 hours evacuation.

Fig. 15-d. Air to the cell.

Fig. 15-e. Air to the cell for 24 hours.

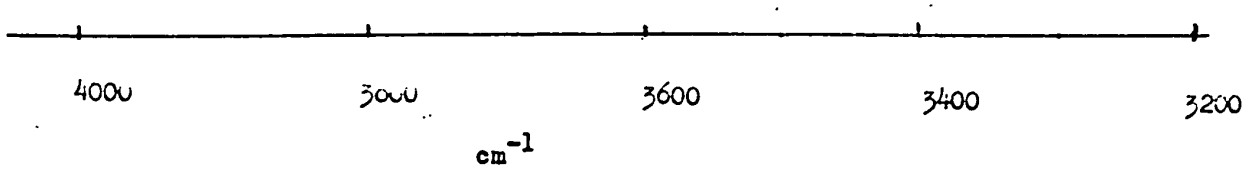


Figure 15. 0.1 mm. $B^{10}F_3$ adsorbed on silica.

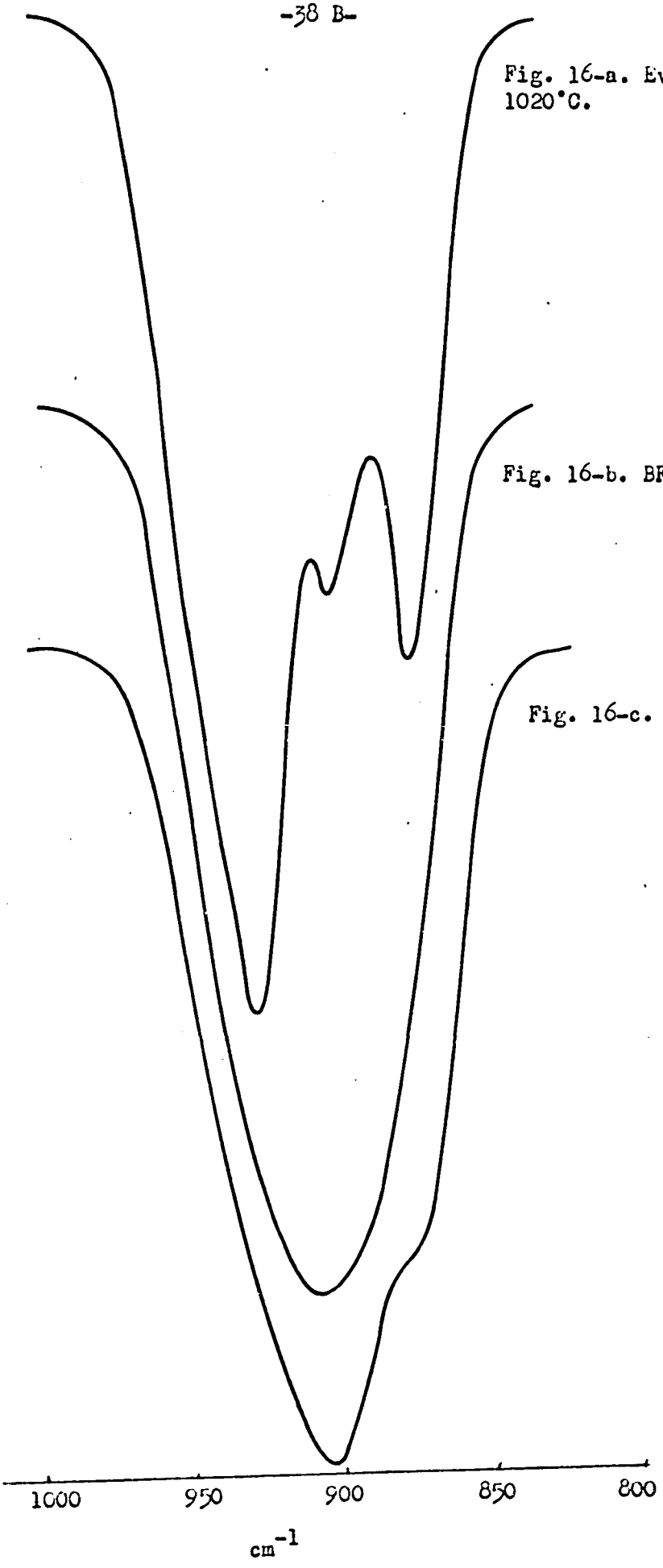


Fig. 16-a. Evacuation at 1020°C.

Fig. 16-b. BF_3 adsorption .

Fig. 16-c. Air to the cell.

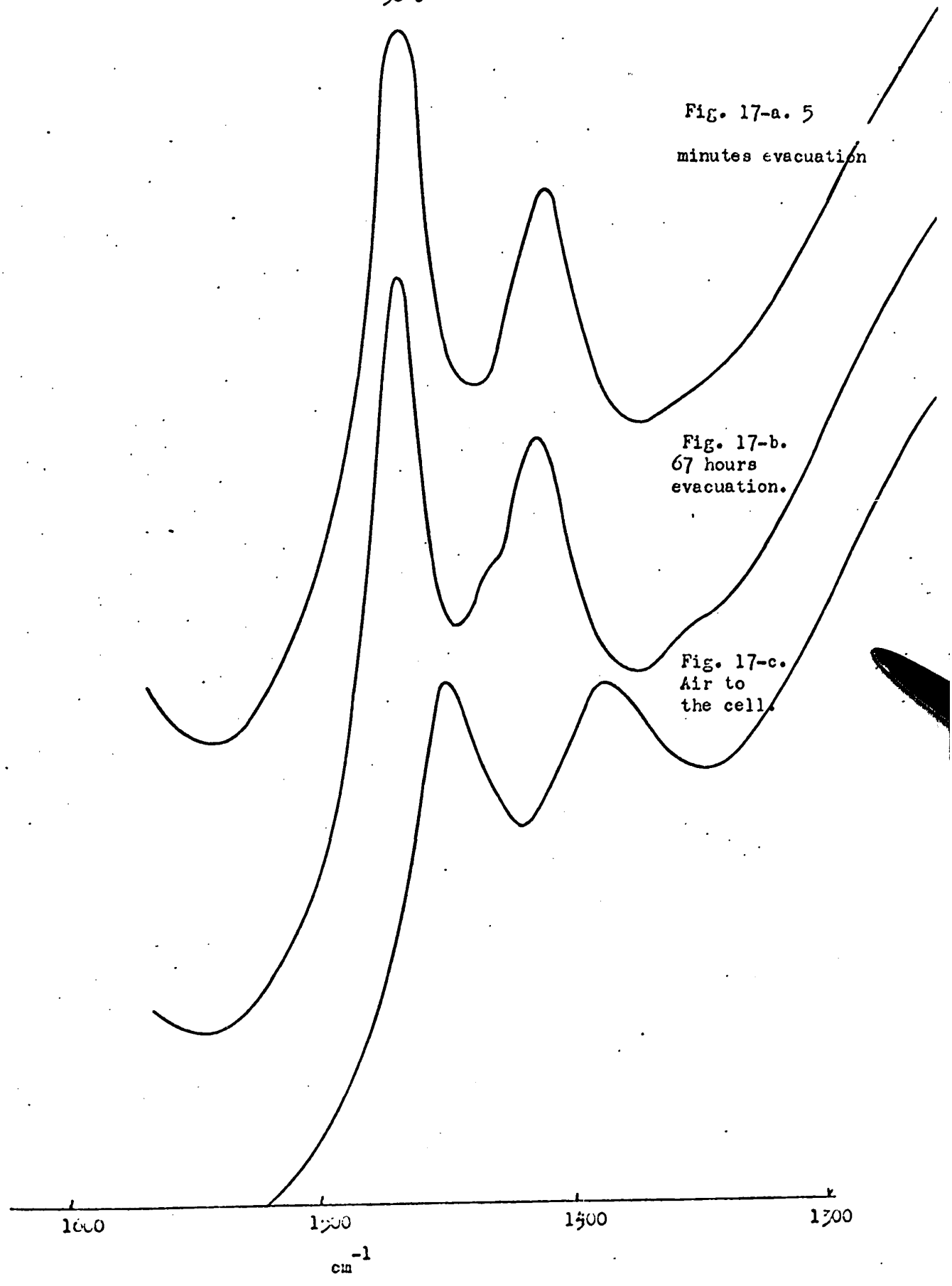


Figure 17. 0.1 mm. $B^{10}F_3$ adsorbed on silica

The Spectra of H_2O^{18} Exchanged Silica Samples

The bulk oxygen atoms of silica are known to exchange with O^{18} labelled water under conditions of high temperatures and pressures.[51] There is no report to date of surface hydroxyls exchanging with H_2O^{18}. It was assumed during the course of this investigation that if the silanol groups did exchange with H_2O^{18}, then the spectrum of a partially exchanged silica disc would exhibit an additional band at a frequency lower than 3749 cm^{-1} due to the O-H stretching vibrations of Si-O^{18}-H groups.

Silica samples preheated at 800°C, where only the sharp strong band due to non-hydrogen bonded silanol was present, were exchanged with H_2O^{18} (98.8% O^{18}) at various temperatures. Each of these samples were exposed to 10 mm. of H_2O^{18} vapour for 10 minutes and the excess H_2O^{18} was evacuated. Repeating this procedure 4 times was sufficient to give the maximum degree of exchange at a given sample temperature, i.e. greater exposure to H_2O^{18} did not produce any further exchange. On adding H_2O^{18} at room temperature, no additional bands were produced in the spectrum. The spectrum of a silica sample exchanged at 200°C showed an additional band at 3738 cm^{-1} that has 2/3 of the intensity of the adjacent 3749 cm^{-1} band (Fig. 18a) indicating that about 40% of the Si-O^{16}-H groups present after evacuating the sample at 800°C had exchanged

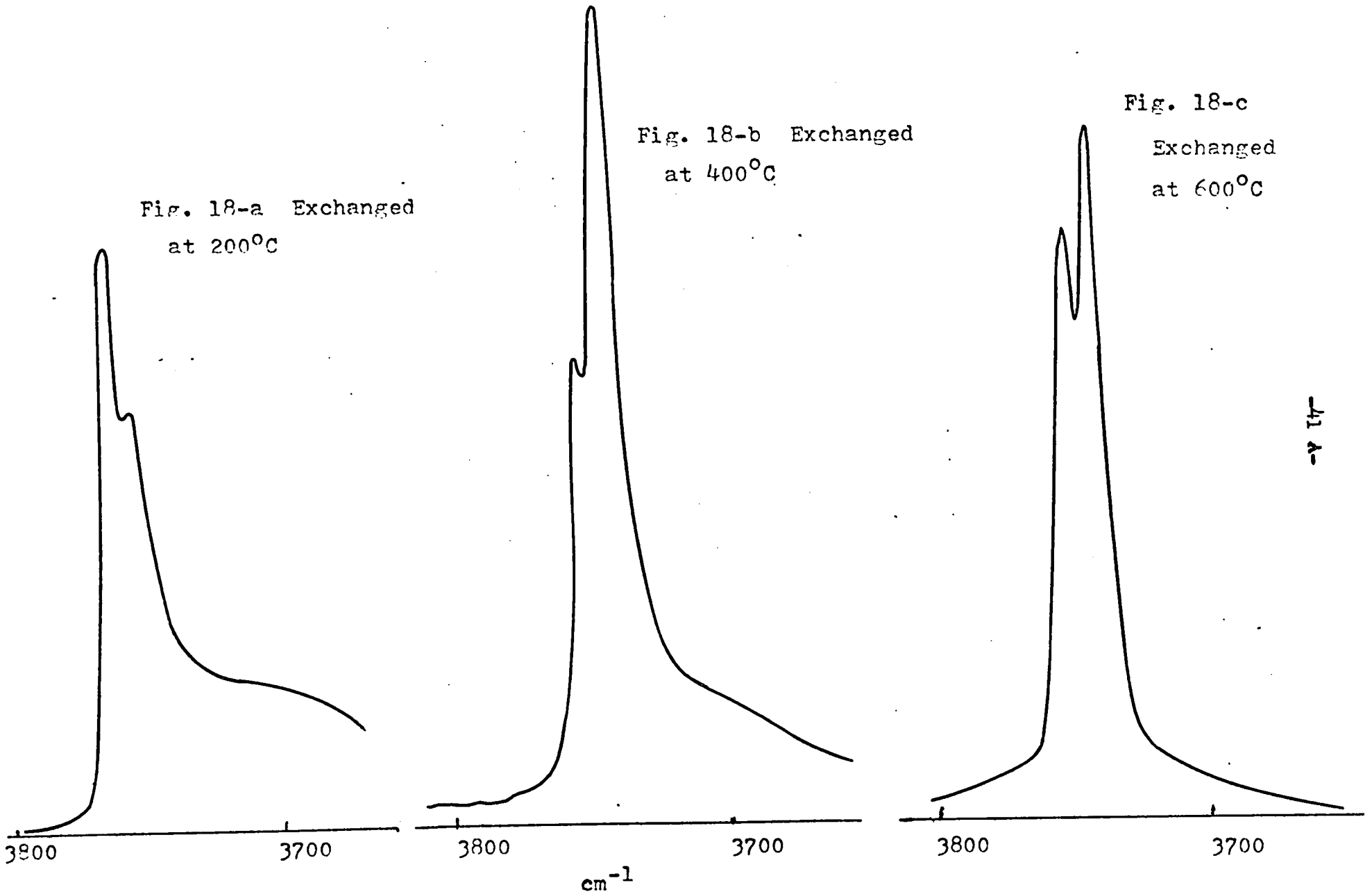
with H_2O^{18} to produce Si-O^{18}-H groups. A maximum exchange of about 70% was obtained at 400°C (Fig. 18b). Beyond 400°C, with increasing temperatures, the percentage exchange appeared to decrease although this may have been due to the fact that at higher temperatures, dehydration processes were probably competing with the exchange reaction. For example, at 600°C, about 55% exchange was obtained (Fig. 18c).

A 60% exchanged sample, which had been evacuated at 800°C prior to H_2O^{18} exchange, was degassed at temperatures from 600-800°C to obtain a spectrum with an almost equal ratio of the 3749 and 3738 cm^{-1} bands (Fig. 19a). On rehydrating this with H_2O^{18} the 3738 cm^{-1} band grew to about 4 times the intensity of the accompanying 3749 cm^{-1} band (Fig. 19b). The intensity of the Si-O^{16}-H band had not changed, indicating that only new O^{18}-H groups had formed and no further exchange of the existing O^{16}-H had taken place. On subsequent evacuation at 800°C, the intensity of the 3738 cm^{-1} band decreased and that of the 3749 cm^{-1} remained unchanged (Fig. 19c). On further evacuation, both the band intensities diminished although the 3738 cm^{-1} band was removed at a faster rate than the 3749 cm^{-1} band. After evacuating the sample at 1020°C for 7 hours, the bands were reduced to a weak doublet (Fig. 19d); in the 1000-800 cm^{-1} region, a strong band at 890 cm^{-1} and a very weak band at 908 cm^{-1} were present.

Fig. 18-a Exchanged at 200°C

Fig. 18-b Exchanged at 400°C

Fig. 18-c Exchanged at 600°C



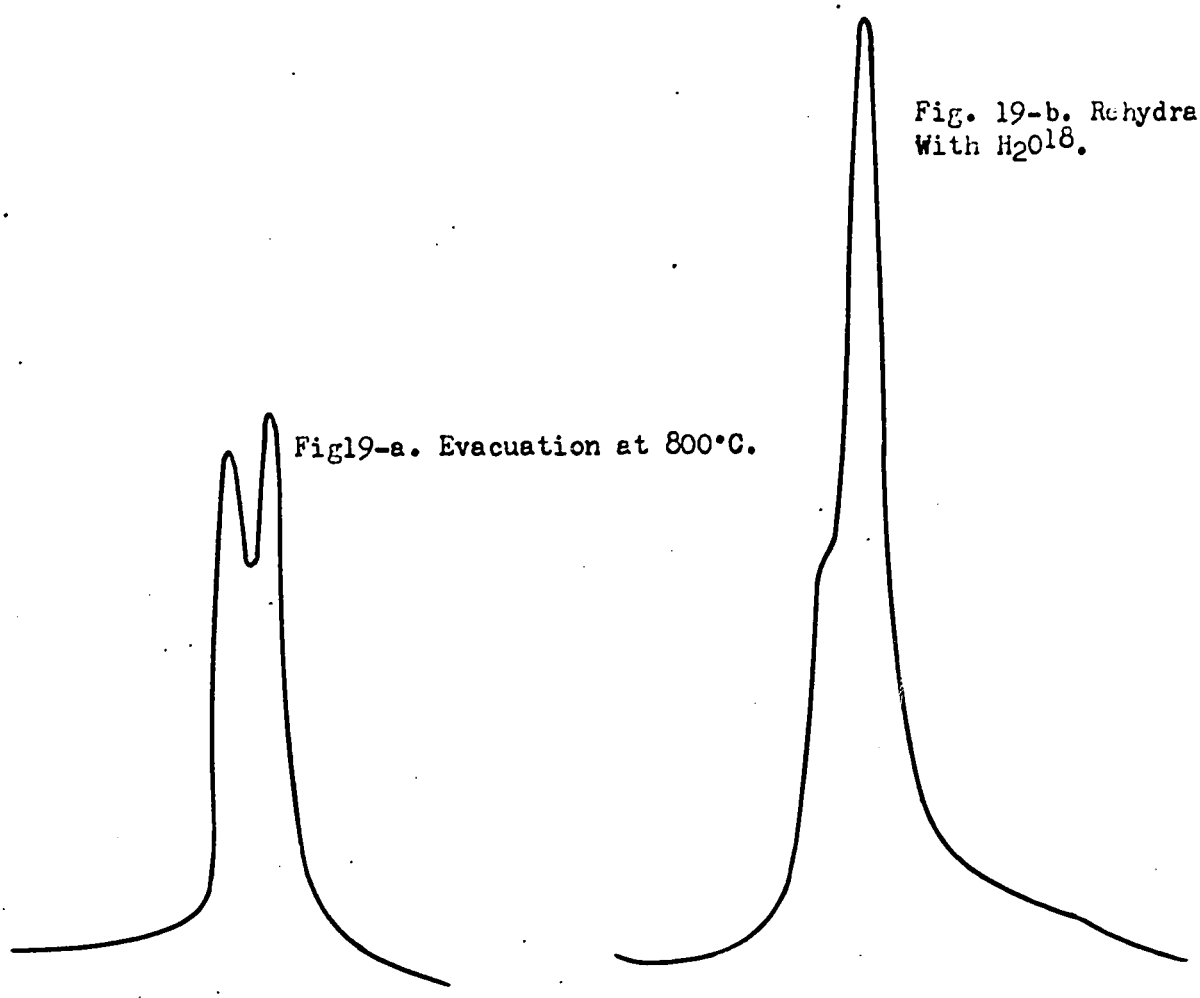


Fig. 19-b. Rehydration With H_2O^{18}.

Fig19-a. Evacuation at 800°C.

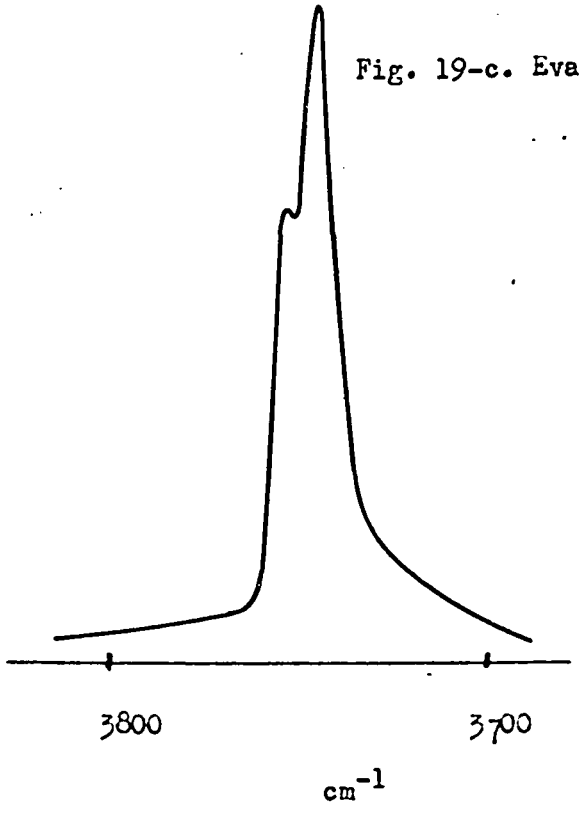


Fig. 19-c. Evacuation at 800°C.

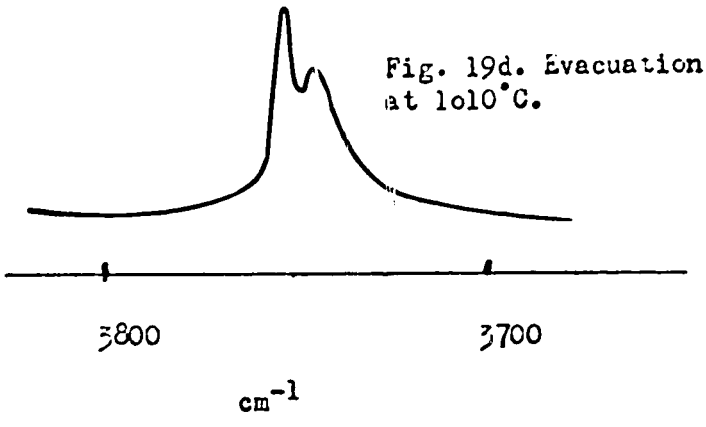


Fig. 19d. Evacuation at 1010°C.

3800 3700

cm^{-1}

3800 3700

cm^{-1}

BF_3 Adsorbed on H_2O^{18} Exchanged Silica Samples

The spectrum of a H_2O^{18} exchanged (at 600°C) silica sample to which 0.5 mm. $B^{10}F_3$ was added for 15 sec. followed by 1 min. evacuation is given in figure 20a. The sample was evacuated at 800°C for 3 hours prior to adsorption. The 1500 cm^{-1} band present in set I_b is split into another less intense band at 1485 cm^{-1}; there are three other bands at 1465, 1448 and 1387 cm^{-1}. On evacuating the sample for 26 hours (Fig. 20b), the 1500, 1485 and 1448 cm^{-1} (Set I_c) band intensities have decreased and the two bands at 1465 and 1387 cm^{-1} (Set II_c) have increased in intensity. The frequencies of the bands in sets II_b and II_c are found to be the same (Figs. 20b, 13d). On adding air to the cell both the sets I_c and II_c bands are replaced by the two bands at 1475 and 1420 cm^{-1} (Set III_c) (Fig. 20c) that were also present in set III_b (Fig. 13e).

B^nF_3: Figure 21-a shows the spectrum of a H_2O^{18} exchanged silica sample to which 0.05 mm. B^nF_3 was added for 10 sec. followed 1 min. evacuation. The sample was evacuated at 800°C for 3 hours following H_2O^{18} exchange. Both the 1500 and 1452 cm^{-1} bands are split to two bands at 1485 and 1434 cm^{-1} respectively; a weak shoulder at 1409 and a band at 1393 are also present. After 26 hours evacuation, the 1500, 1485, 1452, 1434 and 1393 cm^{-1} bands (Set I_d) have decreased in intensity; a more intense 1409 cm^{-1} band and

a band at 1341 cm^{-1} (Set II_d) are present (Fig. 21b). On adding air to the sample, the set II_d bands and the remaining set I_d bands are replaced by two bands at 1425 and 1375 cm^{-1} and a weaker band at 1475 cm^{-1} (Set III_d) (Fig. 21c). The frequencies of the sets II_d and II_a (Figs. 21b and 10d) are sets III_d and III_a (Figs. 21c and 10c) are the same. No further spectral changes were observed on exposing the sample to air for 24 hours in the 1650-1300 cm^{-1} region.

The behaviour of the bands in the 3800-3900 cm^{-1} region were identical for H_2O^{18} exchanged silica samples to which either $B^{10}F_3$ or B^nF_3 had been added. The spectrum of an about 40% exchanged silica sample evacuated at 800°C for 3 hours subsequent to H_2O^{18} exchange contains two bands at 3749 and 3738 cm^{-1} of O.D. 0.2 and 0.08 respectively Fig. (22a). On adding 0.5 mm. B^nF_3 to the same sample, the intensity of the 3749 cm^{-1} band is lowered to O.D. 0.1 and that of the 3738 cm^{-1} band to O.D. 0.03 (Fig. 22b). On evacuating the sample for 26 hours after adding B^nF_3, the 3749 and 3738 cm^{-1} bands have increased to O.D. 0.14 and 0.06 respectively (Fig. 22c). On adding air to the cell, the 3749 cm^{-1} band has grown to O.D. 0.17 and the 3738 cm^{-1} to O.D. 0.08 and an additional band is present at 3700 cm^{-1} of O.D. 0.05 (22-d).

Figure 23a shows the spectrum, in the 3800-3700 cm^{-1} region of a 60% exchanged silica disc that had been evacuated at 600°C for 3 hours following H_2O^{18} exchange. There are

two bands at 3749 and 3738 cm^{-1} of O.D. 0.22 and 0.45 respectively. On adding 0.5 mm. $B^{10}F_3$ to the cell, the 3749 cm^{-1} band is lowered to O.D. 0.11 and the 3738 cm^{-1} band to O.D. 0.25 (Fig. 23b). On 60 hours evacuation, the 3749 and 3738 cm^{-1} bands have grown to O.D. 0.19 and 0.39 respectively (Fig. 23c). The spectral behaviour of the bands in figures 22 and 23 indicate that both the 3749 and 3738 cm^{-1} grow on evacuating a H_2O^{18} exchanged silica after BF_3 adsorption, i.e. the apparent growth of the weaker band is not effected by the real growth of the stronger band.

There were no bands in the 1000-800 cm^{-1} region after adding either $B^{10}F_3$ or B^nF_3 to a H_2O^{18} exchanged silica sample or on subsequent evacuation. However, in both cases, on exposing the sample to air a band at 880 cm^{-1} was always produced.

The frequencies of the bands produced on adding $B^{10}F_3$ and B^nF_3 to H_2O^{18} exchanged silica samples are listed in table 2.

Table 2

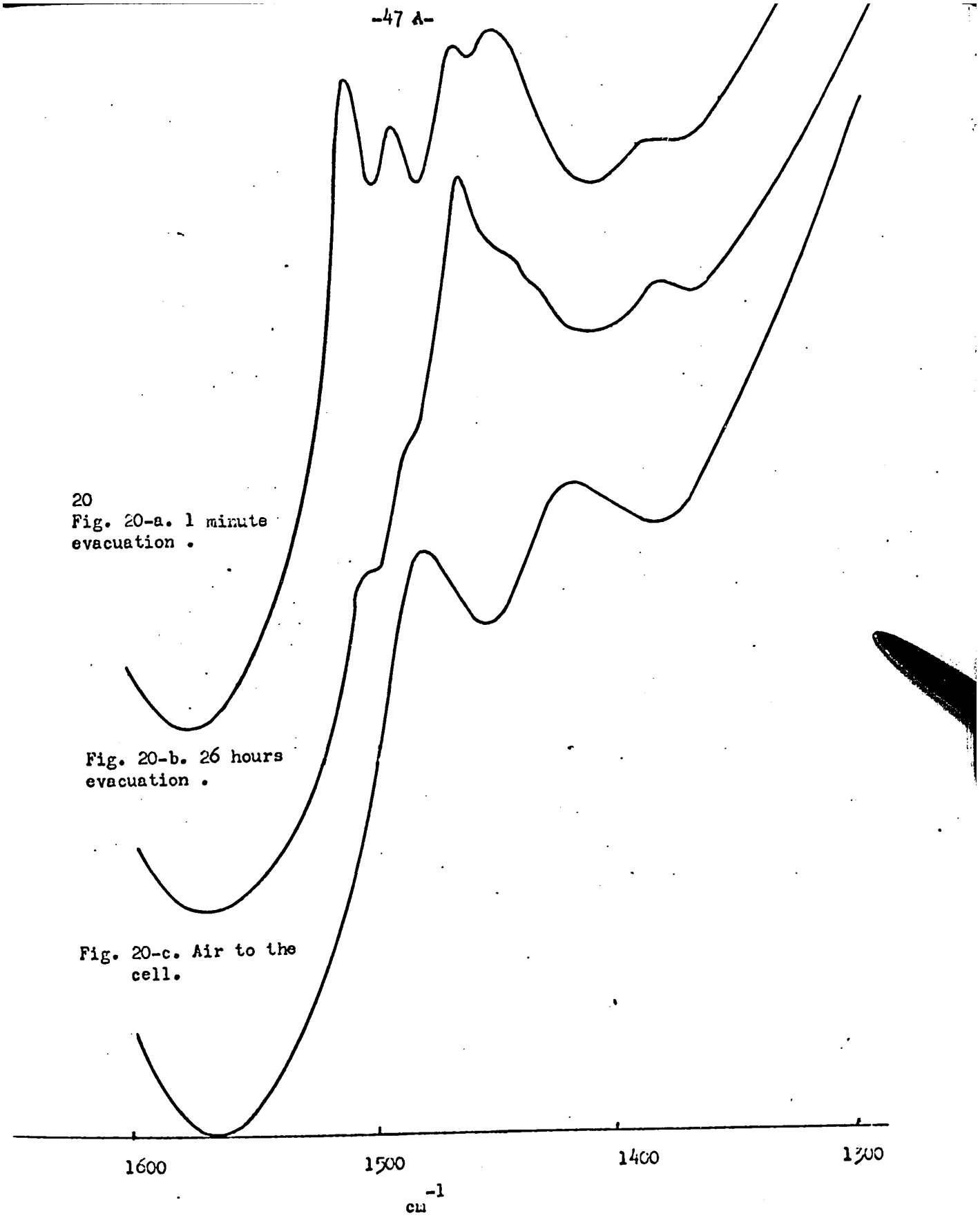
Adsorbate	Set No.	Frequency cm^{-1}
$B^{10}F_3$	I_c	1500, 1485, 1448
$B^{10}F_3$	II_c	1465, 1387
$B^{10}F_3$	III_c	1475, 1420
B^nF_3	I_d	1500, 1485, 1452, 1434, 1393
B^nF_3	II_d	1409, 1341
B^nF_3	III_d	1475, 1425, 1375

Figure 24a shows the spectrum in the 1650-1300 cm^{-1} region of a silica sample to which 0.1 m.m. $B^{10}F_3$ has been added for 30 seconds. The sample was evacuated at 1020°C for 7 hours prior to adsorption. There are three bands present at 1500, 1485 and 1448 cm^{-1} (Set I_c). On evacuation, the set I_c bands decrease very slightly and a pair of extremely weak bands at 1465 and 1387 cm^{-1} (Set II_c) are produced (Fig. 24b). After adding air, the set I_c and II_c bands at 1475 and 1420 cm^{-1} (Set III_c) (Fig. 24c).

The spectral changes in the 3800-3700 cm^{-1} region are shown in figures 25a-d. The intensity of the weak doublet at 3749 cm^{-1} (O.D. 0.02) and the 3738 cm^{-1} (O.D. 0.02), present in the background spectrum (Fig. 25a) does not change in intensity on adding $B^{10}F_3$ to the cell (Fig. 25b). After 58 hours evacuation, the doublet has grown very slightly in intensity to O.D. 0.03 (Fig. 25c). On adding air to the sample both the 3749 and 3738 cm^{-1} bands have grown to O.D. 0.08 and another band at 3700 cm^{-1} (O.D. 0.08) is produced (Fig. 25d). The intensities of the 3749, 3738 and 3700 cm^{-1} bands do not change from those in figure 25d after exposing the sample to air for 24 hours.

The background spectrum of the sample exhibits a strong band at 890 cm^{-1} and possibly a shoulder at 908 cm^{-1} (Fig. 26a) both of which are removed (Fig. 26b) on adding BF_3; no other bands appear in this region during evacuation; on adding air a band at 880 cm^{-1} is produced (Fig. 26c) together with the set III_c bands.

It is seen, from the spectra presented in this chapter, that the bands in the subsets a,b,c and d in each set behave identically under various experimental conditions. There subsets will therefore be referred to only by their set numbers. For example, the bands in set I_a, I_b, I_c and I_d will be collectively termed as set I etc.



20
Fig. 20-a. 1 minute evacuation .

Fig. 20-b. 26 hours evacuation .

Fig. 20-c. Air to the cell.

Figure 20. 0.5 mm. $B^{10}OF_3$ adsorbed on H_2O^{18} exchanged silica.

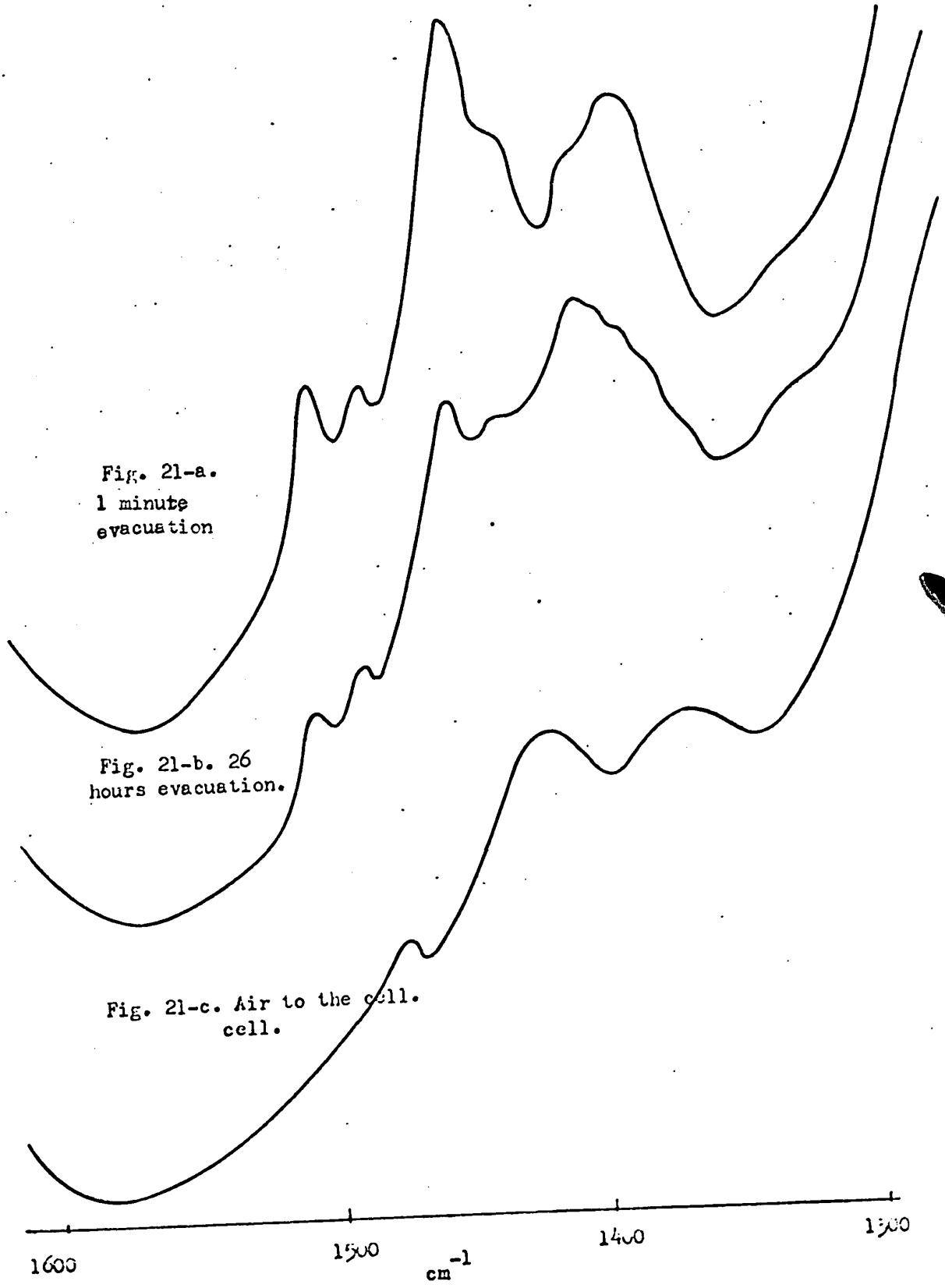


Figure 21. 0.05 mm. B^nF_3 adsorbed on H_2O^{18} exchanged silica.

Fig. 22-a. Evacuation at 800°C.

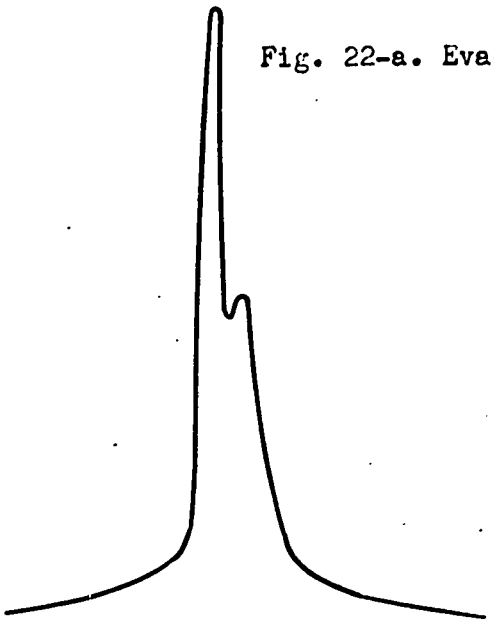


Fig. 22-b. 0.5mm B^nF_3.

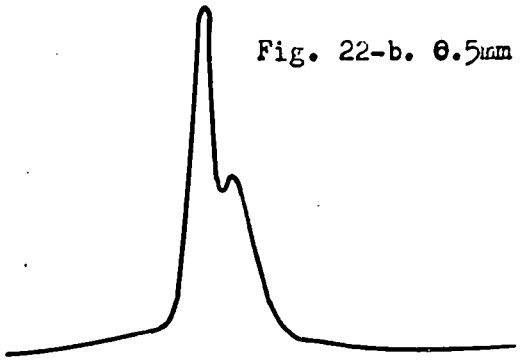


Fig. 22-c. 26 hours evacuation.

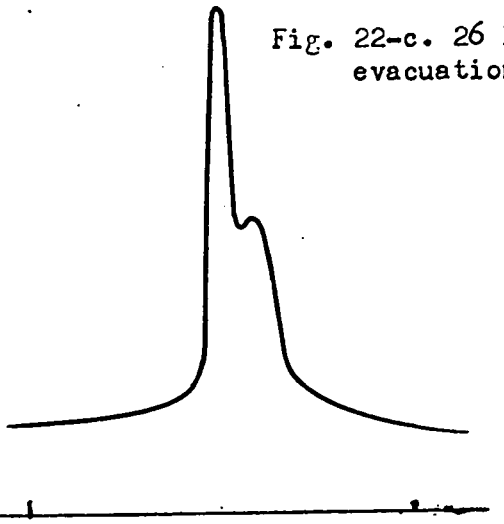


Fig. 22-d. Air to the cell.

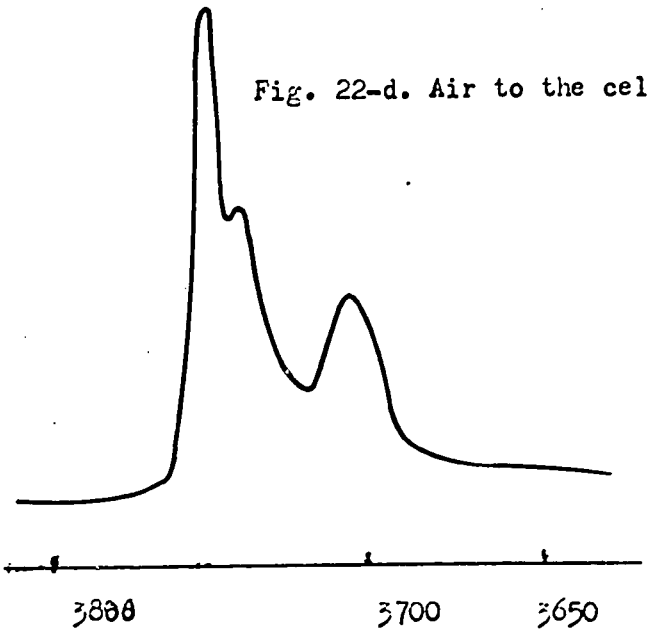


Figure 22. 0.5mm. B^nF_3 adsorbed on H_2O^{18} exchanged silica.

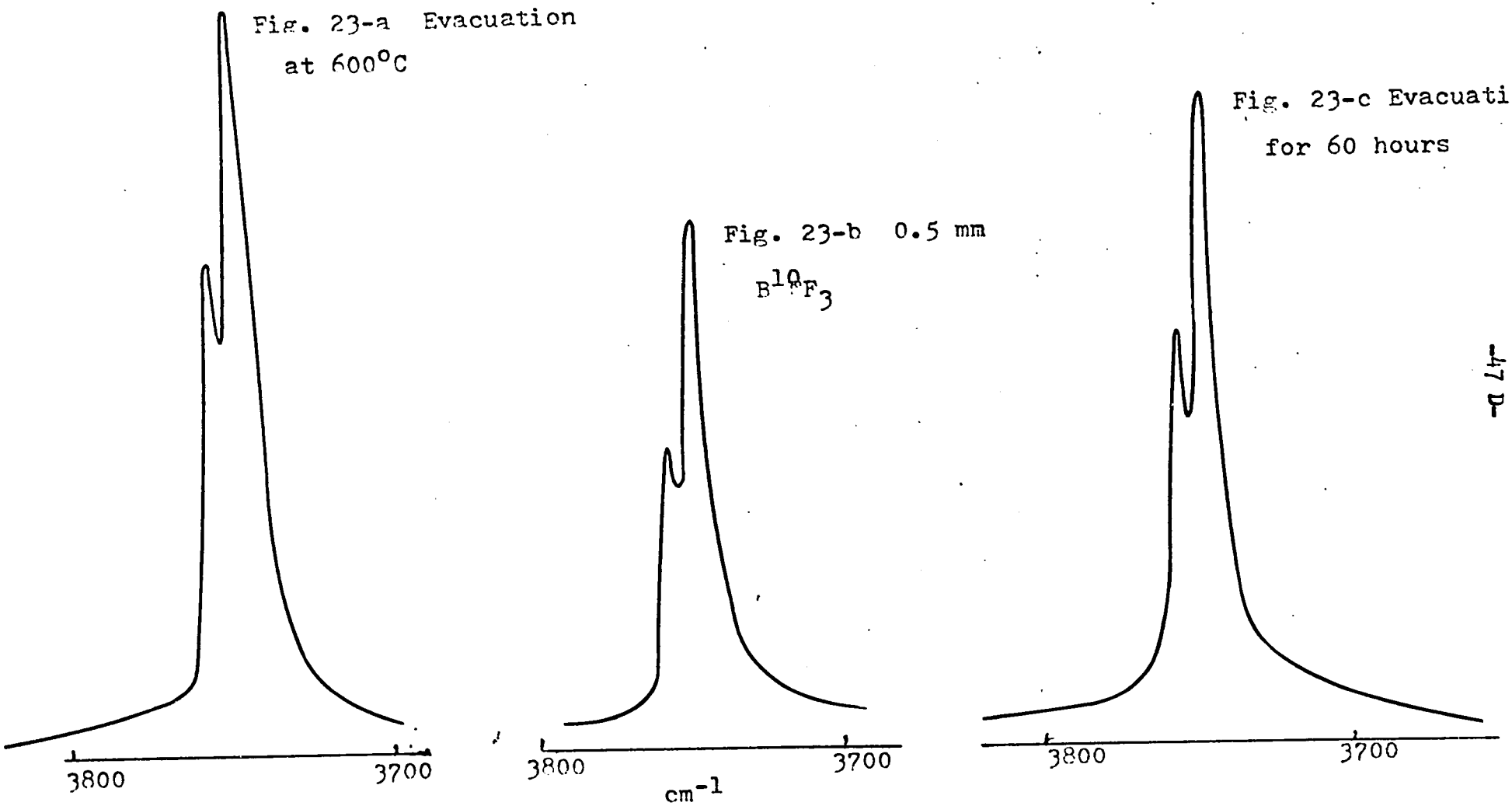


Fig. 23 0.5 mm $B^{10}F_3$ adsorbed on H_2O^{18} exchanged silica

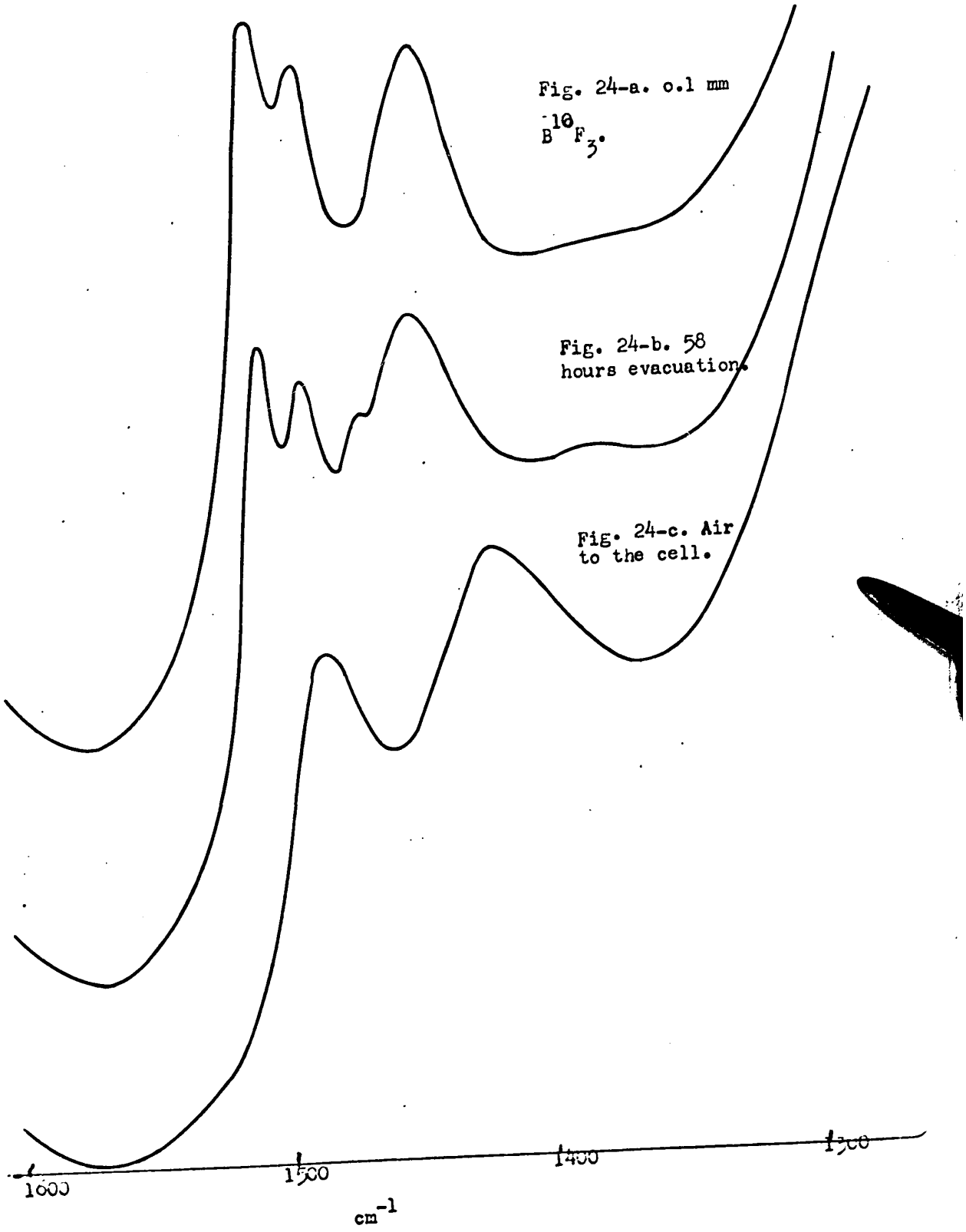


Figure 24. O.1mm. $B^{10}F_3$ adsorbed on H_2O^{18} exchanged silica

Fig. 25-a. Evacuation at 1020°C.

Fig. 25-b. 0.1 mm. $B^{10}F_3$.

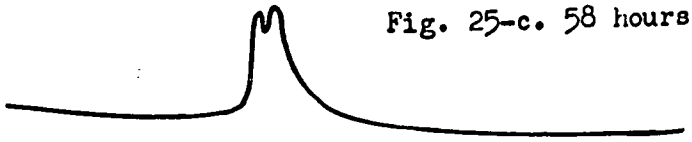


Fig. 25-c. 58 hours evacuation.

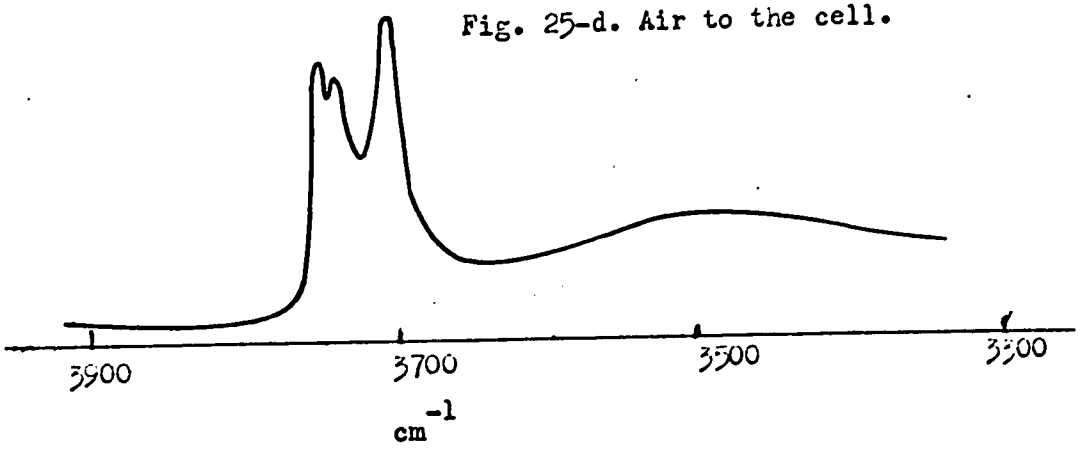


Fig. 25-d. Air to the cell.

Figure 25. 0.1 mm. $B^{10}F_3$ added to H_2O^{18} exchanged silica.

Fig. 26-a. Evacuation at 1020°C.

Fig. 26-b. 0.1mm. $B^{10}F_3$.

Fig. 26-c. Air to the cell.

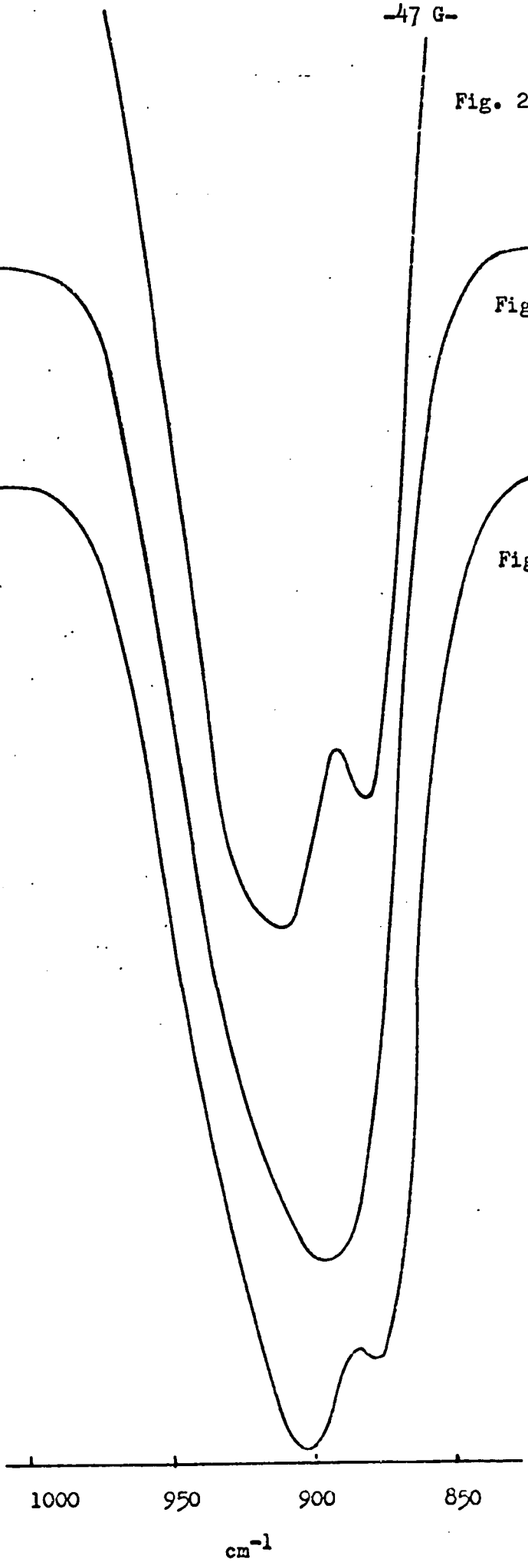


Figure 26. o.1 mm. $B^{10}F_3$ adsorbed on H_2O^{18} exchanged silica.

DISCUSSION

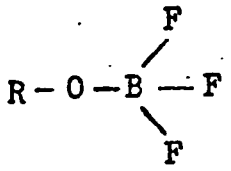
Boron trifluoride, adsorbed on silica

In the recent work by Rhee and Basilla, [47] the infrared spectra obtained after the adsorption of BF_3 on silica samples which havebeen previously evacuated at 500°C were similar to those obtained in this work. The two initial bands at 1500 and 1450 cm^{-1} were assigned to the doubly degenerate B-F asymmetric stretching modes of planar $B^{10}F_3$ and $B^{11}F_3$ respectively:

A third band at 1392 cm^{-1} that did not disappear on evacuation was assigned to the B-O stretching mode of $O-BF_2$. They also observed an initial disappearance of the 3749 cm^{-1} due to the O-H stretching vibration of Si-O-H and its subsequent regeneration on evacuation. However, no explanation of this was given that would concur with the proposed mechanisms. Although the asymmetric stretching modes of planar gaseous $B^{10}F_3$ and $B^{11}F_3$ do exhibit bands at 1504 and 1453 cm^{-1} respectively, [52] it is hard to imagine why BF_3 after being adsorbed on the silica surface should still retain its planarity. Further, the stability on evacuation of the set A bands produced after adding BF_3

to silica samples heated at temperatures greater than 1000°C suggests that the bonds between the surface and the initial species are possibly stronger than those formed on physical adsorption. The splitting of the 1500 and 1453 cm^{-1} bands on adsorbing BF_3 to aH_2O^{18} exchanged silica observed in these investigations (Fig. 21a) proves conclusively that these two bands cannot be attributed to the BF_3 stretching modes.

Boron trifluoride on reacting with electron donating molecules generally forms adducts via the B:O coordinate bond where the planar BF_3 becomes pyramidal: (53)



A sample of these compounds e.g. $(CH_3)_2O$: BF_3, $(CH_3)_2$ N:BF_3 and their corresponding B-F and B-X (X = O, N) vibrational frequencies are given in Table 3. The B-O stretching mode of a B-O coordinate bond occurs in the 600-680 cm^{-1} region. The boron oxygen double bond (B=O) and the B-O single bond stretching frequencies occur near 2000 cm^{-1} and in the 1400-1300 cm^{-1} regions respectively (Table 4).

However, Moor and Kelen (54) have reported that BF_2 asymmetric stretching and B-O stretching modes of difluoroboric acid methyl ester (F_2 $BOCH_3$) occur at 1385 and 1420 cm^{-1} respectively; the latter band is at a frequency higher than the

TABLE 3

Infrared stretching frequencies of some BF_3 adducts

Adduct	B-F sym. str.[a] cm^{-1}	B-F asym. str.[b] cm^{-1}	B-X str. cm^{-1}	Ref.
$(CH_3)_2\ O{:}B^{10}F_3$	810	1259	672	(71)
$(CH_3)_2\ O{:}B^{11}F_3$	805	1216	661	(71)
$(C_2H_5)_2\ O{:}B^{10}F_3$	758	1210 1252	678	(72)
$(C_2H_5)_2\ O{:}B^{11}F_3$	756	1163 1210	664	(72)
$CH_3\ NH_2{:}BF_3$	956	1190	718	(73)
$(CH_3)_3\ N{:}BF_3$	930	1139	692	(73)

(a) symmetrical stretch

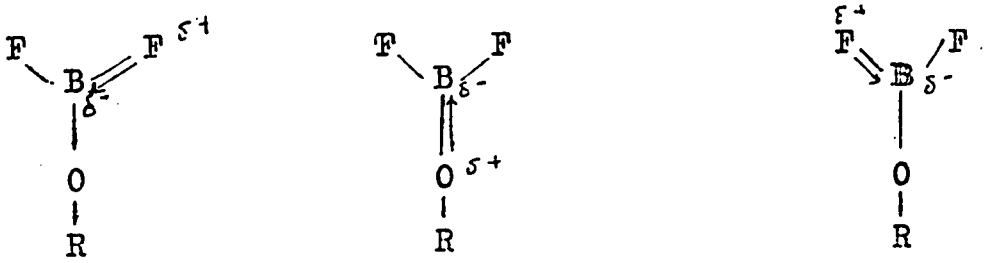
(b) asymmetrical stretch

TABLE 4

B-O stretching frequencies of some boron and oxygen containing compounds

Compound	B-O sym. str. cm^{-1}	B-O asym. str. cm^{-1}	B=O str. cm^{-1}	Ref.
$B(OCH_3)_3$	727	1361		(74)
$HB(OCH_3)_3$	1270	1360		(74)
$Cl\ B(OCH_3)_2$	1277	1372		(75)
$Cl_2\ B(OCH_3)$	1355			(75)
$Cl-B<^{OCH_3}_{C_6H_5}$	1350			(64)
$C_6H_5B(OH)_2$		1355		(76)
HBO_2		1420	2030	(77)
$B_2{}^{10}O_3$	760	1270	2087	(78)
$B_2{}^{11}O_3$	757	1268	2021	(78)

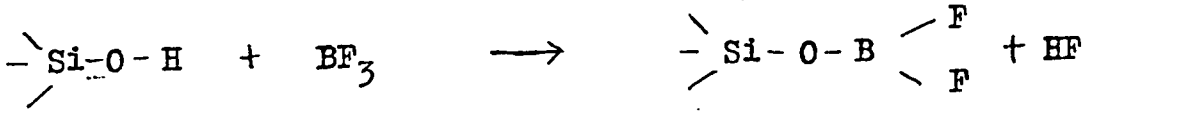
frequencies of B-O single bond stretching modes of other boron and oxygen containing compounds(Table 4). The authors have proposed that the B-O bond order of this compound is 1-1/3 due to adifference in the electronegativities of the fluorine and oxygen atoms. The compound has the following mesomeric structures:



(a) (b) (c)

Of these structures (b) should predominate since oxygen is less electronegative than fluorine giving the B-O bond an enhanced double bond character.

A similar type of surface species (to be called species A) may also form initially by the following reaction when gaseous BF_3 is adsorbed on silica containing single surface hydroxyls :



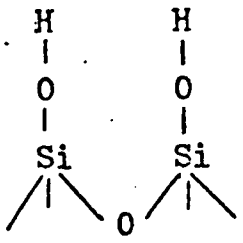
(A) (1)

The BF_2 symmetrical and asymmetrical stretching modes of CH_3BF_2 and FCH_2BF_2[55] have neen assigned at 1250(sym.)

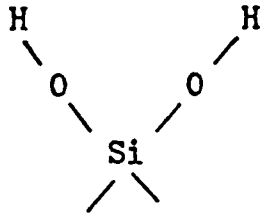
and 1360 (asym) cm^{-1} and 1244 (sym) and 1410 (asym) cm^{-1} respectively. A surface OBF_2 group has three stretching modes: the BF_2 symmetrical stretching band can be expected to lie in the 1200 cm^{-1} region; whereas, the B-O stretch and the asymmetrical BF_2 stretch would be observed in the 1500-1350 cm^{-1} region.

The frequencies of the set I bands produced on adding BF_3 to silica lie in the 1500-1400 cm^{-1} region (Table 1) and can possibly be assigned to the vibrational modes of such a OBF_2 group. The observed splitting of the 1500 and 1452 cm^{-1} bands into bands at 1485 and 1434 cm^{-1} respectively produced in the spectra of BF_3 adsorbed on H_2O^{18} exchanged silica indicates that these two bands in set I are attributable to oxygen containing groups. Of the two vibrational modes that may produce the bands in Set I, the $B\text{-}O^{16}$ stretching mode can therefore be assigned to the 1500 (B^{10}) and 1452 cm^{-1} (B^{11}) bands and the 1485 and 1434 cm^{-1} bands can be assigned to the corresponding $B\text{-}O^{18}$ stretching modes. The two other bands in set I at 1448 and 1393 cm^{-1} can possibly be assigned to the asymmetric stretching modes of $B^{10}F_2$ and $B^{11}F_2$ respectively.

On the assumption that the set I bands can be assigned to species A, ($SiOBF_2$) several additional reactions can be postulated which can account for the observed spectral changes on prolonged evacuation. Silica samples evacuated at lower temperatures may contain a large number of adjacent (i) and geminal (ii) hydroxyl groups. (17,(36)

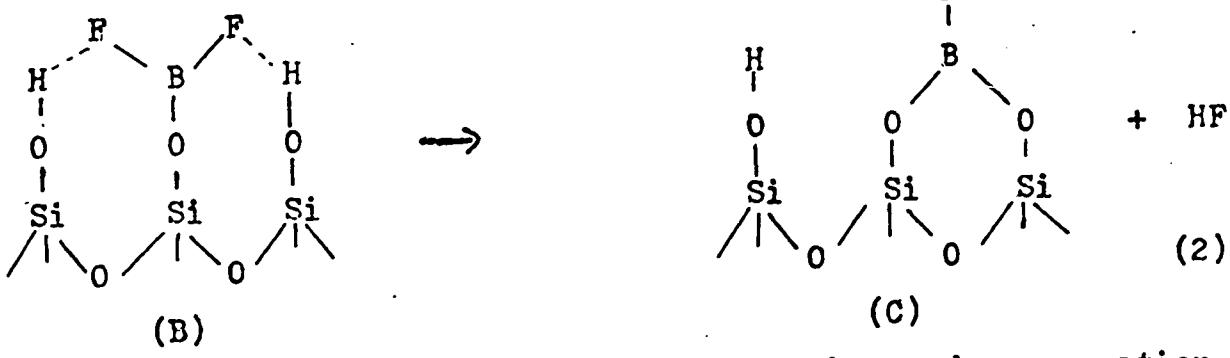


(i)



(ii)

The surface hydroxyls may either react with BF_3 to give species A or may hydrogen bond with the remaining two fluorine atoms to give a species B. The formation of species B, therefore, could cause the initial removal of the 3749 cm^{-1} Si-O-H band. The intermediate species B might further react to form a species C via reaction 2 releasing a non-hydrogen bonded silanol group:

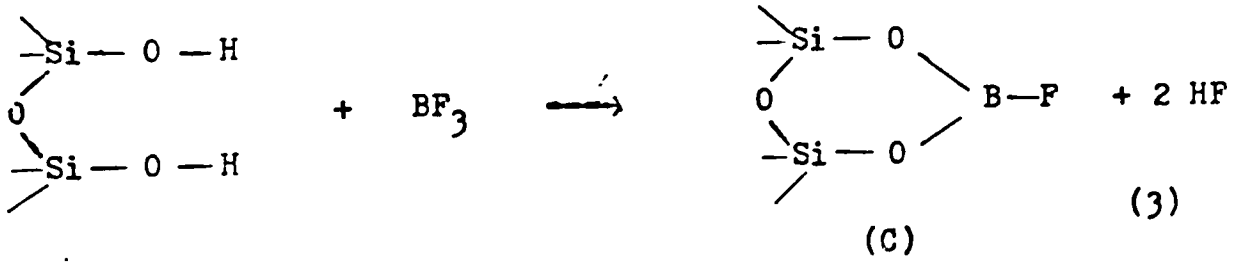


(B) (C) (2)

Reaction (2) would then result in the observed regeneration of the initially removed Si-O-H band at 3749 cm^{-1} and the replacement of the set I bands by a new set of bands produced by the vibrational modes of species C. The set II bands, that increase in intensity with the simultaneous growth of the Si-O-H band at 3749 cm^{-1} and the decrease in set I band intensities, may be

assigned to the vibrational stretching frequencies of the FBO_2 group in species C. The asymmetric BO_2 stretching vibrations of cyclic B, O compounds occur in the 1500-1400 cm^{-1} region, whereas, the symmetrical BO_2 stretching vibrations occur in the 1200-1010 cm^{-1} region (Table 4). The B-F stretching vibrations of trifluoroboroxine $(BOF)_3$ and mixed halide boroxines $B_3O_3Cl_2F$ have been assigned at 1387 and 1371 cm^{-1} respectively [56] (Table 4). The 1465 (B^{10}) and 1409 (B^{11}) cm^{-1} bands are possibly due to the assymetric stretching mode of BO_2 and those at 1387 (B^{10}) and 1341 (B^{11}) are due to the B-F stretching modes of species C. That the spectra of the H_2O^{18} exchanged silica sample treated with BF_3 do not exhibit any splitting of the 1465 and 1409 cm^{-1} bands assigned to the BO_2 stretching modes is not so unexpected since the isotopic shift in cyclic compounds may be quite small. Further, the bands due to asymmetric stretching vibrations of $BO_2{}^{18}$ and $O^{16}BO^{18}$ of O^{18} substituted species C may be overlapping with the $BO_2{}^{16}$ bands or with the adjacent bands assigned to the stretching vibrations of BF_2 and BF groups.

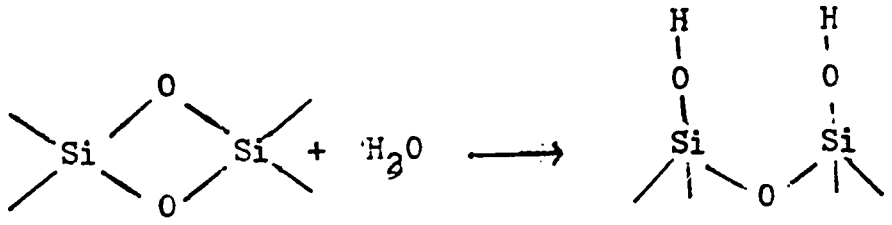
Boron trifluoride may also react directly with the adjacent hydroxyls present on low temperature heated silica surfaces to form species C (reaction 3).



(C) (3)

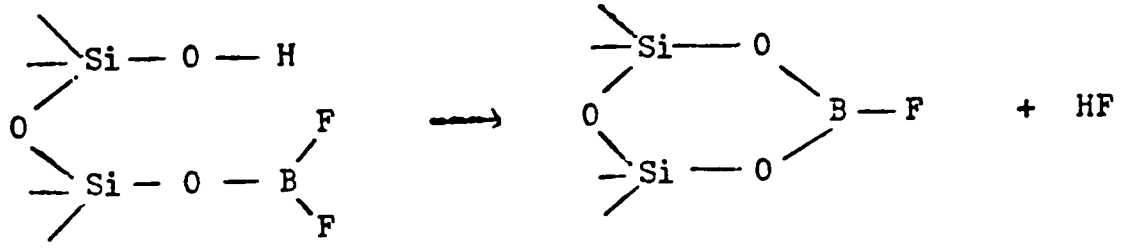
On such samples, the set II bands are also observed initially along with the stronger set I bands due to the possible simultaneous formation of species C and species A via reactions (3) and (1) respectively.

The observed growth of the 3749 cm^{-1} band, on evacuating a silica disc at room temperature that had been previously dehydrated at 950°C in order to partially remove the 3749 cm^{-1} band (Fig. 7), suggests that a certain amount of "H_2O" or "OH" groups are available during evacuation. This small amount of "H_2O", the origin of which will be discussed later, possibly reacts with the Si-O-Si groups formed on dehydration to produce SiOH groups (reaction 4).



(4)

Some of these SiO-H groups may also react with a neighboring species A to form species C via a reaction similar to reaction (5) with a possible resultant conversion of set I bands to set II bands.

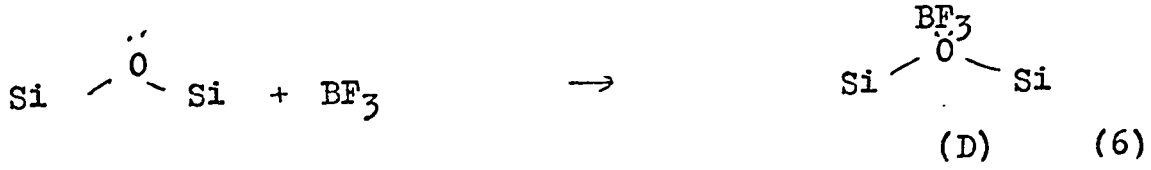


(A) (C)

(5)

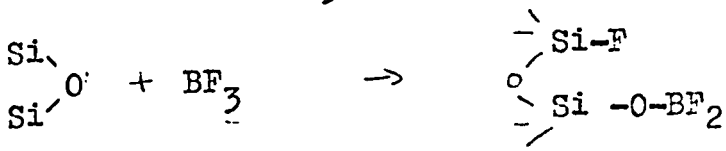
On reacting BF_3 on silica samples which had been evacuated at temperatures greater than 1000°C where a small number of single hydroxyls and possibly no adjacent hydroxyls are present, only s species A may be produced initially. In the absence of adjacent OH groups, reaction 2 can possibly no longer take placeso that the set I bands may not be converted to set II bands. The "excess H_2O" which may also be available to high temperature heated surfaces, may form Si-O-H groups via reaction4. The small degree of rehydrationof the surface can therefore result in the observed growth of the Si-O-H band and the formation of very weak setII bands during evacuation.

BF_3 may form an adduct with the Si-O-Si group via reaction 6.



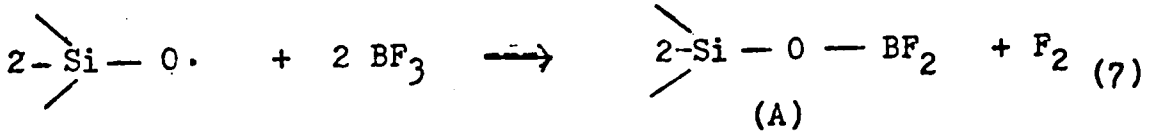
(D) (6)

The existence of species D cannot be readily verified since the B:O stretching vibrations and the B-F symmetric and asymmetric modes lie in the 600-680, 700-810 and in the 1140-1260 cm^{-1} regions respectively, (table 3). BF_3 can further react via the following reaction:

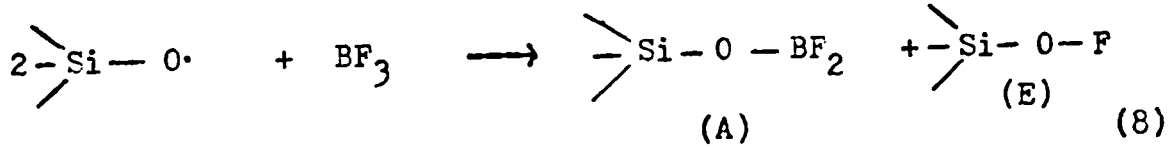


The two strong bands at 908 and 890 cm^{-1} present in the spectrum of high temperature heated silica, whose intensities vary directly with the temperature of dehydration and the

degree of removal of the 3749 cm^{-1} band, may be attributed to the Si-O vibrations of strained Si-O-Si bridges or to surface Si-O· free radicals. The diminished intensity of the 908 cm^{-1} band observed in the spectrum of high temperature heated H_2O^{18} exchanged silica indicates that at least one of these may be caused by an oxygen containing species. E.S.R. data have shown that surface free radicals are produced on silica which have been dehydrated at high temperatures. (57) The disappearance of the 908 and 890 cm^{-1} bands on adding BF_3 may be due to the formation of species A and species E via reactions 7 and 8 respectively.



(7)



(8)

The O-F stretching frequencies in OF_2, O_2F, O_4F_2 and O_2F_2 are found to occur in the 822-554 cm^{-1} region. (58)

In another type of reaction, proposed by Basilla and Rhee, (47) species of the type $MOBX_2$ react with M-O-M sites (where M = Si; X = halides) to produce M-X (reactions 9, 10).

$$M-O-BX_2 \quad + \quad M-O-M \longrightarrow \quad M-O-\overset{\overset{X}{|}}{B}-O-M \quad + \quad MX \qquad (9)$$

(A) (C)

$$M_2O_2-BX \quad + \quad M-O-M \longrightarrow \quad M-O-\overset{\overset{M}{|}}{\underset{\underset{O}{|}}{B}}-O-M \quad + \quad MX \qquad (10)$$

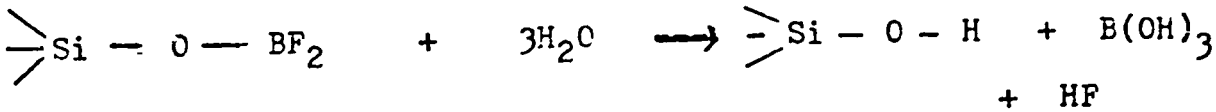
(C) (F)

For the analogous reaction with BF_3 and SiO_2, replace X by F and M by Si. The Si-F stretching frequencies lie between 1000 and 800 cm^{-1} region (59); of this the 950-850 cm^{-1} region is transparent to infrared radiation against a silica background. However, the observed absence of any infrared band in the later region, after evacuation, does not necessarily discount the possibility for reactions (9) and (10) since the surface Si-F frequency may have shifted to a slightly lower or higher value and have become undetectable. However, if reaction (9) were to take place, the species (A) produced on surfaces with very small amounts of Si-O-H should still be converted to species C, i.e. set I bands should change to set II bands. Secondly, the conversion of species C to species F via reaction (10) would be accompanied by the replacement of set II bands by a new set of bands. As neither of the above changes is observed in the infrared spectrum of silica samples reacted with BF_3, it is quite possible that reactions (9) and

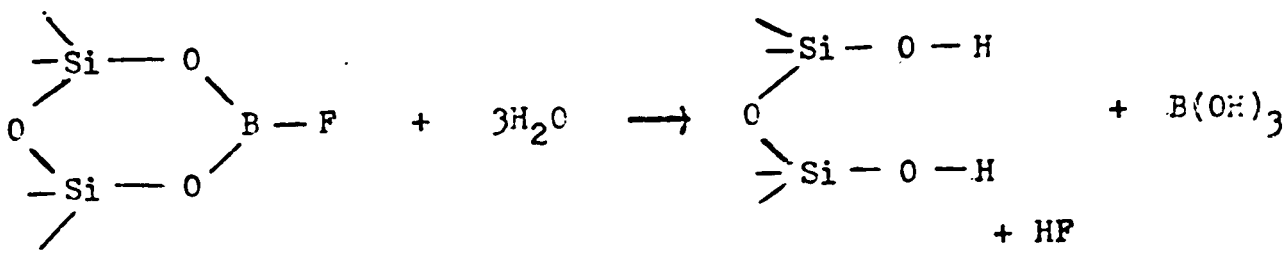
(10) do not also take place on the surface.

Boron trifluoride may also be physically adsorbed and the fluoride atoms of these molecules may weakly hydrogen bond with the Si-O-H groups on the surface. On evacuation, the BF_3 molecules may either desorb from the surface thereby releasing the Si-O-H groups or react to produce either species A or C.

The set III bands that occur in the same frequency range as the B-O stretching vibrations may be assigned to the various boron oxygen containing species produced on adding air. Matossi and Bluschke [60] have reported a band at 1470 cm^{-1} due to B-O stretching mode of boric acid; Bethell and Sheppard [61] have assigned this band at 1450 cm^{-1}. Servoss and Clark [62] reports that the spectra of $B^{10}(OH)_3$ and $B^{11}(OH)_3$ exhibit bands at 1490 and 1428 cm^{-1} respectively and a band at 882 cm^{-1} which has no isotopic shift. The 1475, 1425 and 880 cm^{-1} bands observed on adding air to BF_3 treated silica samples may be attributed to boric acid which is possibly one of the hydrolyzed products (reactions 11 and 12).



(11)



(12)

The 3700 cm^{-1} band produced on adding air is due to the formation of free B-O-H groups. On greater contact with air, these free B-O-H groups hydrogen bond with neighboring hydroxyl groups or with physically adsorbed water to produce the observed decrease in the 3700 cm^{-1} band. The observed frequencies and their corresponding vibrational modes of the possible surface species formed on adsorbing BF_3 on silica are listed in table 5.

TABLE 5

Observed frequencies of BF_3 adsorbed on silica

Frequency obs. cm^{-1}	Assignment	Species
3749	O^{16}-H str.	Si-O^{16}-H
3738	O^{18}-H str.	Si-O^{18}-H
3700	O^{16}-H str.	B-O^{16}-H
1500	O^{16}-B^{10} str.	O^{16}-B^{10}-F_2
1485	O^{18}-B^{10} str.	O^{18}-$B^{10}F_2$
1452	O^{16}-B^{11} str.	O^{16}-$B^{11}F_2$
1434	O^{18}-B^{11} str.	O^{18}-$B^{11}F_2$
1448	B^{10} (F, F) asym. str.	O-B^{10}-F_2
1393	B^{11} (F, F) asym. str.	O-B^{11} F_2
1465	O, O, B^{10} asym. str.	O_2B^{10}-F
1409	O, O, B^{11} asym. str.	O_2B^{11}-F
1387	B^{10}-F str.	O_2B^{10}-F
1341	B^{11}-F str.	O_2B^{11}-F

RESULTS

Boron trichloride adsorbed on silica

Although the BCl_3 adsorption experiments were initially carried out to aid the band assignments in the previous experiments, it was found that the position and the spectral behaviour of the bands produced after adsorbing BCl_3 on silica were different from those observed after adsorbing BF_3 on silica. Figure 27a shows the spectrum of a silica sample to which 1.5 mm B^nCl_3 was added for 15 seconds followed by 2 minutes evacuation. This sample had been evacuated at 800°C for 6 hours prior to BCl_3 adsorption. Initially, a strong band at 1365 cm^{-1} (Set IVa) and a shoulder at 1430 cm^{-1} are produced (Fig. 27a). On evacuating the sample for 23 hours, the set IV a band intensities have decreased; a weak shoulder at 1325 cm^{-1} together with a broad band containing peaks at 1455, 1428 and 1410 cm^{-1} and very weak shoulders at 1470 and 1455 cm^{-1} (Set Va) are also present (Fig. 27b). After 43 hours evacuation, the set IVa bands are almost removed and the intensities of the set Va bands have increased (Fig. 27c). On adding air to the cell after 44 hours evacuation, a broad unresolved band is observed in the 1480 to 1370 cm^{-1} region (Fig. 27d); on exposing the sample to air for longer period, the set IVa and set Va bands are replaced by two strong bands at 1420 and 1375 cm^{-1} and a weak band at 1475 cm^{-1} (Set VIa) (Fig. 27e).

The spectra of the same sample in the 3800-3200 cm^{-1} region are given in figures 28 a-f. The strong 3749 cm^{-1} band (O.D. 0. 54), present in the background spectrum (Fig. 28a), is lowered to O.D. 0.01 on adding B^nCl_3 to the silica sample. After evacuating the sample for 23 hours following B^nCl_3 adsorption, the 3749 cm^{-1} band intensity is increased slightly to O.D. 0.02 and an additional more intense (O.D. 0.18) at 3700 cm^{-1}, characteristic of the OH vibrational mode of B-OH groups, is produced (Fig. 28c). On subsequent evacuation, both the 3749 and the 3700 cm^{-1} bands grow as the band intensities of the set Va increase and those of set IVa decrease. After 43 hours evacuation, the set IVa bands have almost disappeared and the intensities of the 3749 and 3700 cm^{-1} bands have grown to O.D. 0.06 and 0.28 respectively (Fig. 28d). On adding air to the cell, the 3749 cm^{-1} band intensity has grown to O.D. 0.43 and the 3700 cm^{-1} band intensity is lowered to O.D. 0.2; an additional broad band at 3230 cm^{-1} is also produced (Fig. 28e). On exposing the sample to air for 24 hours, the bands at 3749 cm^{-1} (O.D. 0.42), 3230 cm^{-1} and at 3700 cm^{-1} (O.D. 0.15) are observed (Fig. 28f).

The spectral behaviour of the bands in the 1000-800 cm^{-1} region is shown in figures 29a-e. On adsorbing 1.5 mm. B^nCl_3, a band at 928 cm^{-1}, a stronger band at 952 cm^{-1} and a weak shoulder at 913 cm^{-1} are observed (Fig. 29a) together with the set IVa bands (Fig. 27a). On subsequent evacuation, the intensities of the 952, 928 and 913 cm^{-1} bands decrease

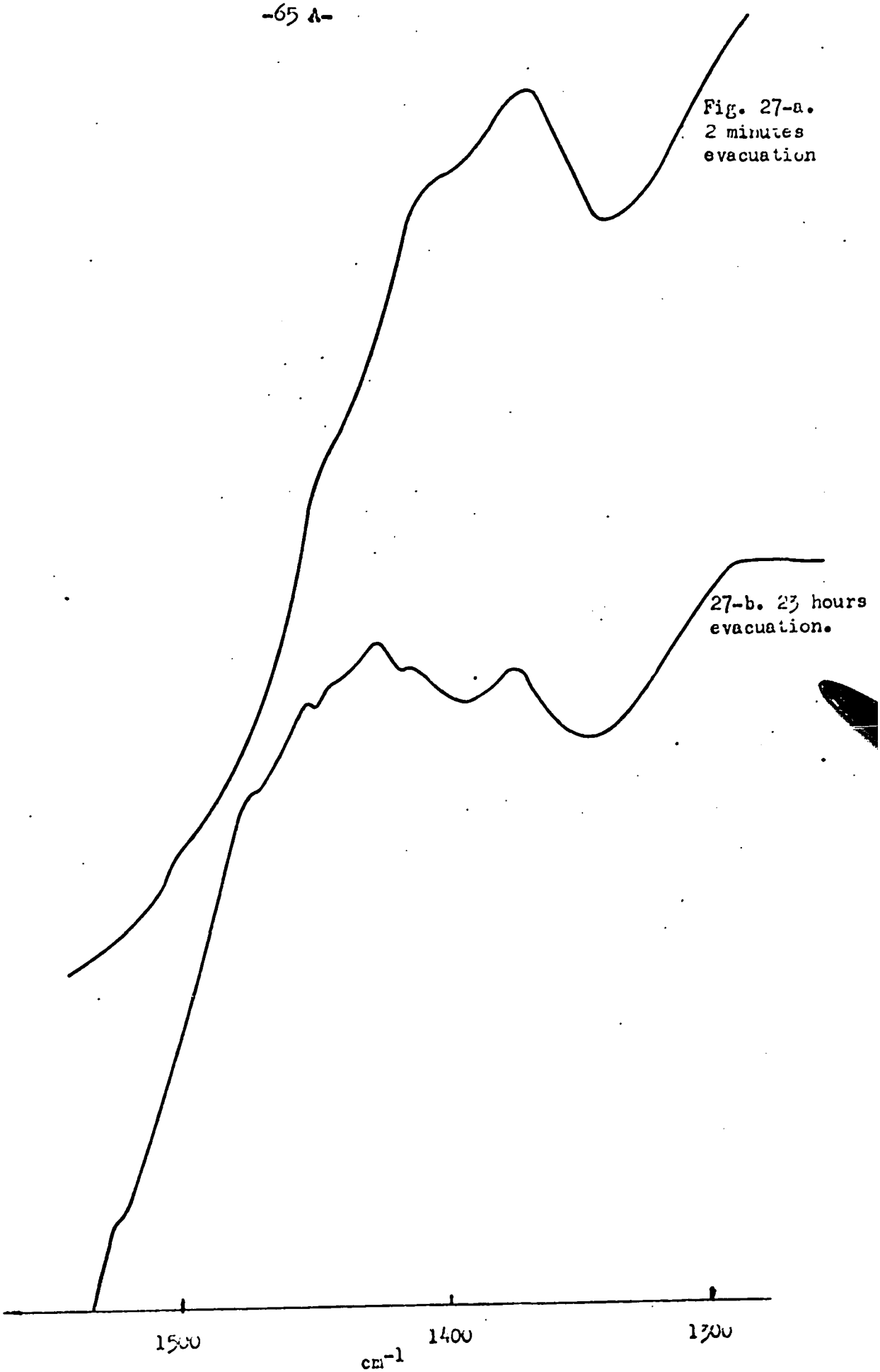


Figure 27. 1.5 mm BCl_3 adsorbed on silica.

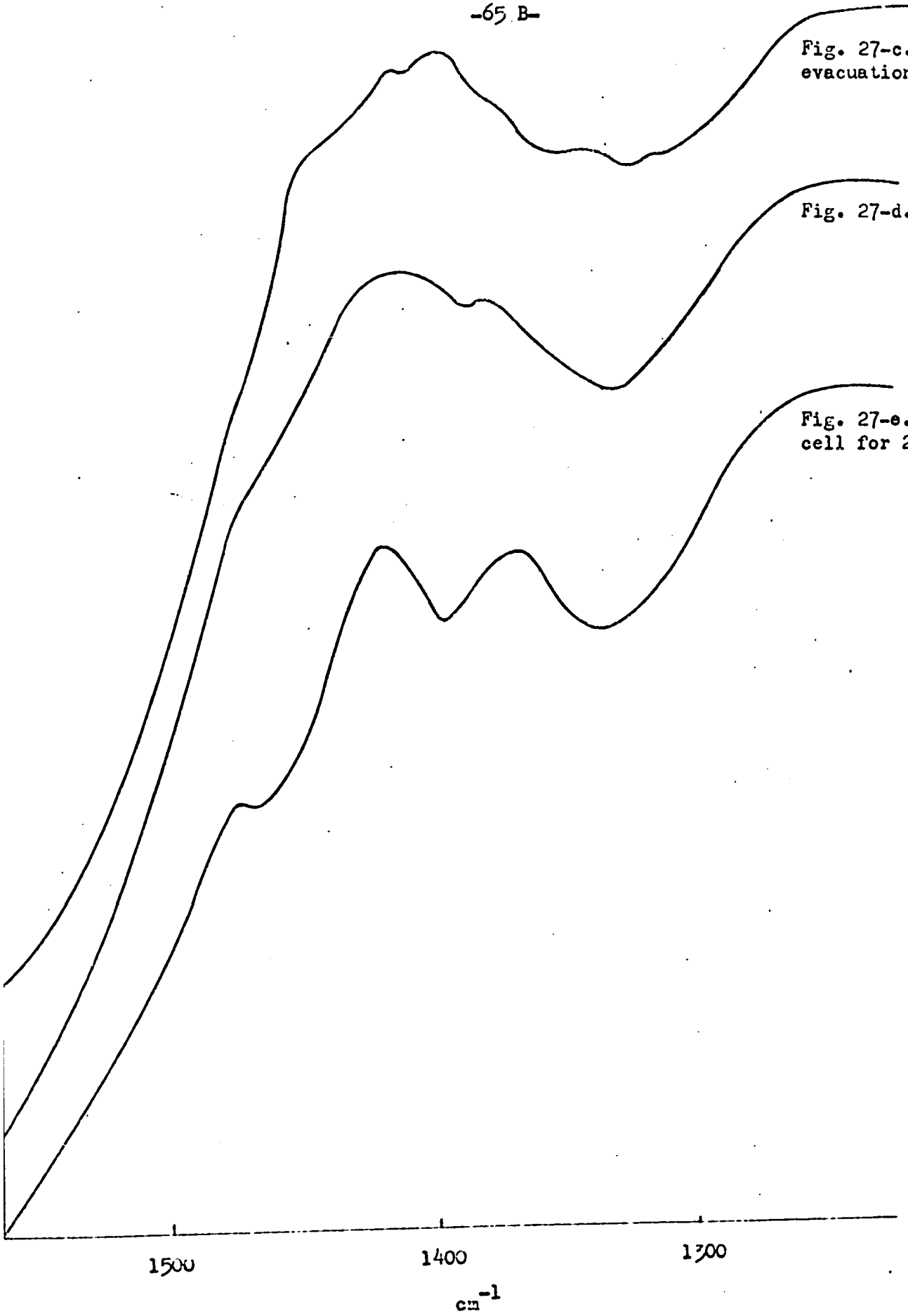


Fig. 27-c. 43hours evacuation.

Fig. 27-d. Air to the cell.

Fig. 27-e. Air to the cell for 24 hours.

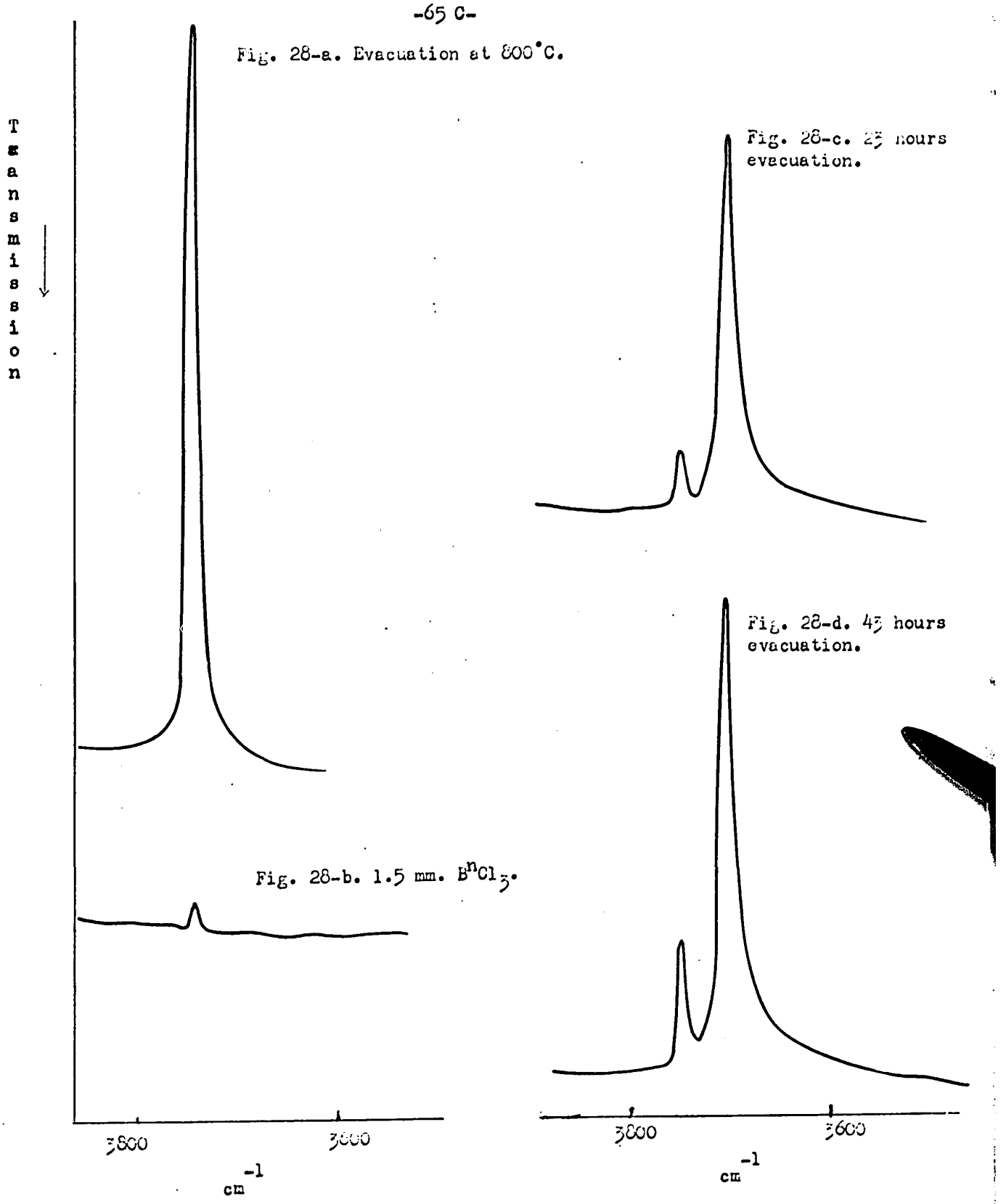


Fig. 28-a. Evacuation at 600°C.

Fig. 28-b. 1.5 mm. B^nCl_3.

Fig. 28-c. 23 hours evacuation.

Fig. 28-d. 43 hours evacuation.

Figure 28. 1.5 mm. B^nCl_3 adsorbed on silica.

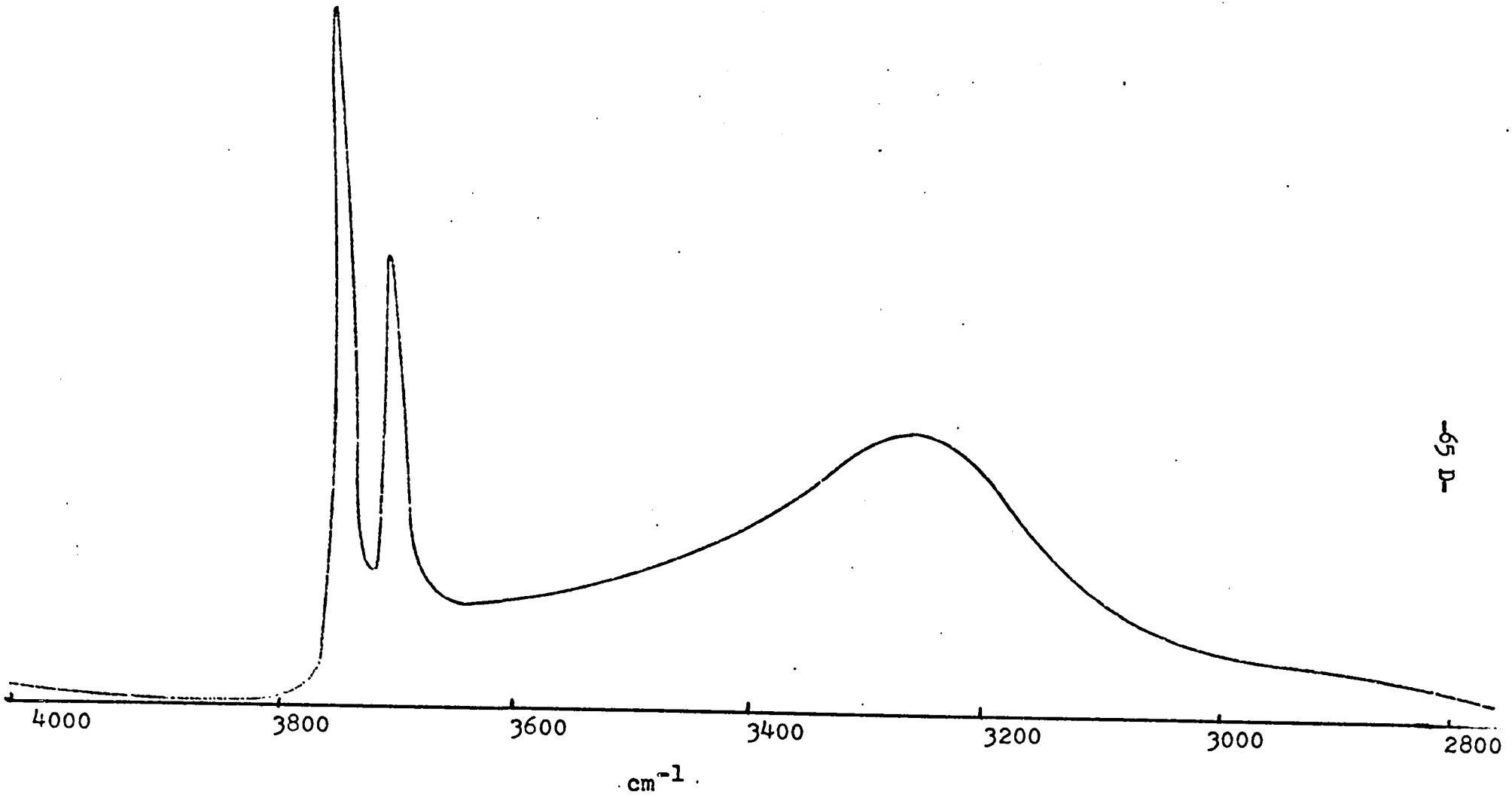


Fig. 28-e Air to the cell

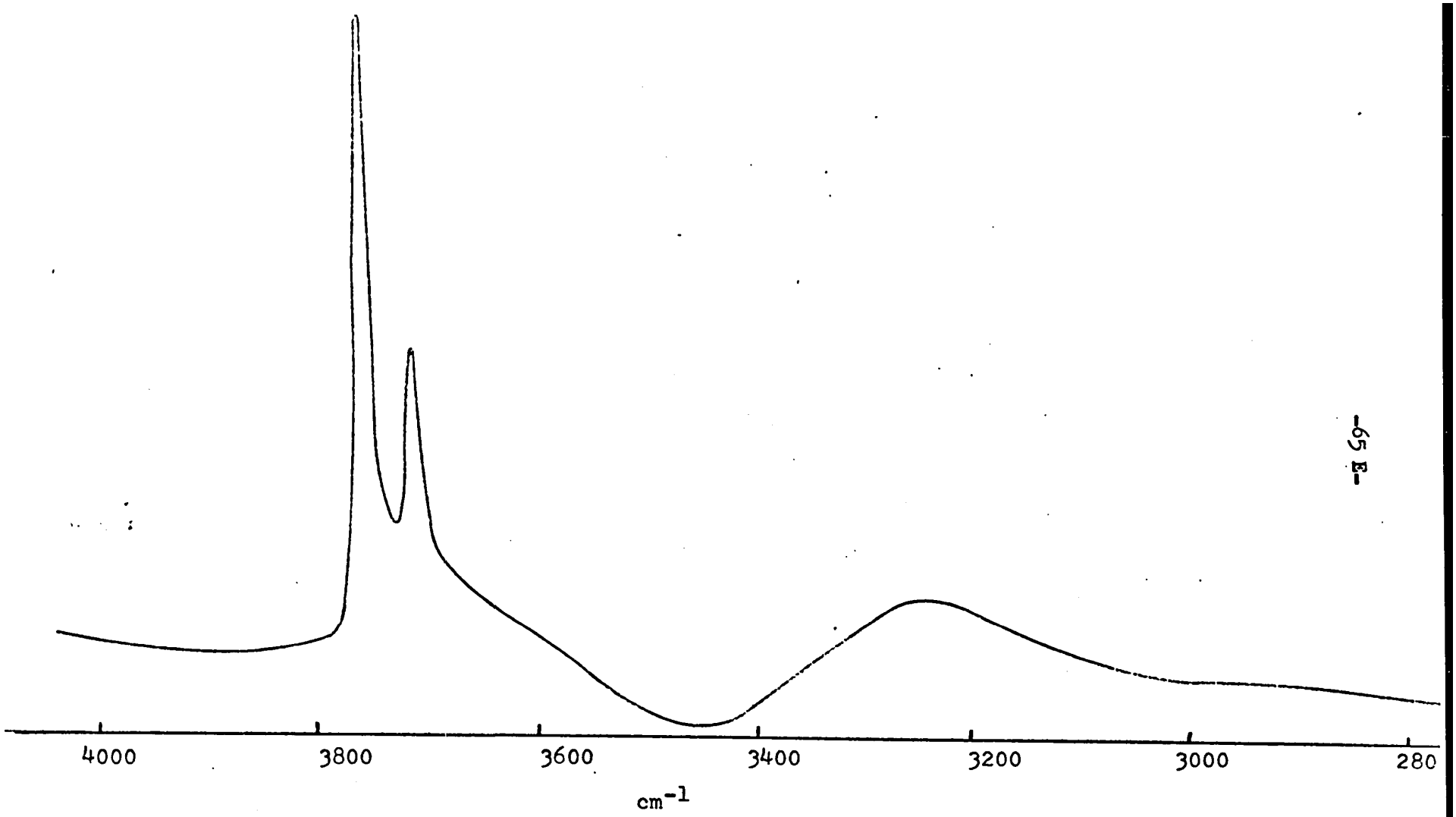


Fig. 28-f Air to the cell for 24 hours

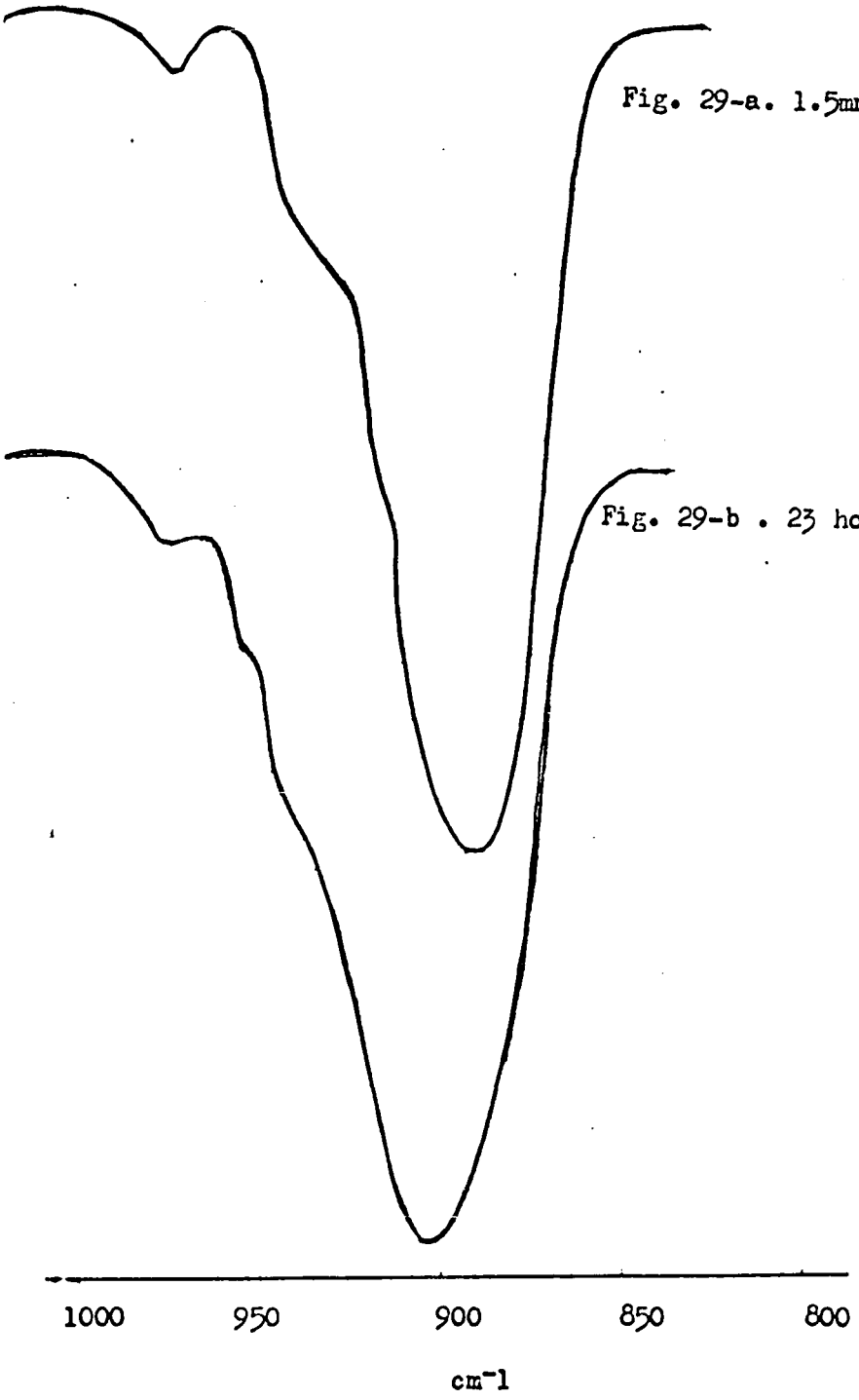


Figure 29. 1.5 mm. B^nCl_3 adsorbed on silica.

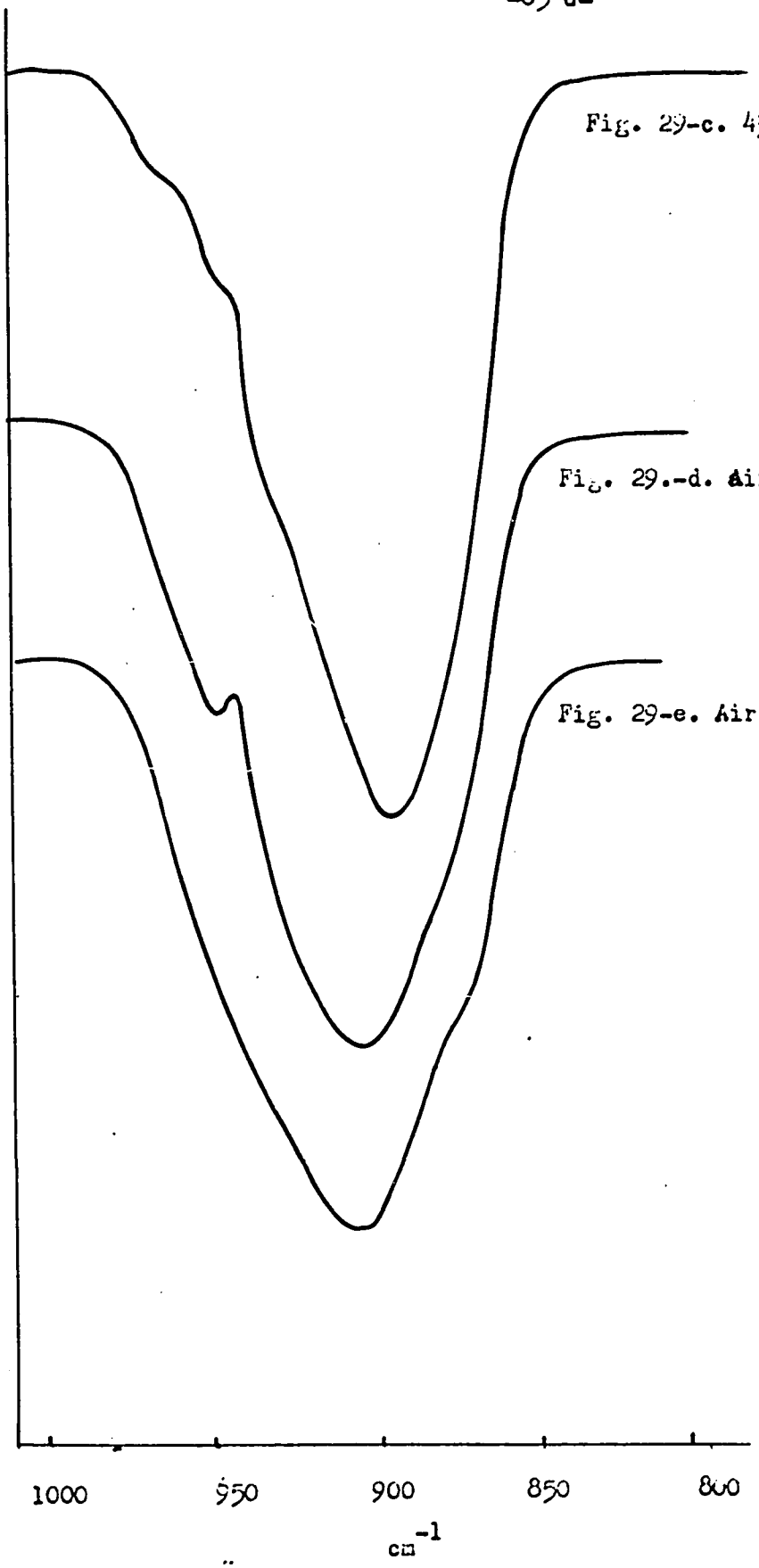


Fig. 29-c. 43 hours evacuation.

Fig. 29.-d. Air to the cell.

Fig. 29-e. Air to the cell 24 hours.

(Fig. 29b-c) as the set Va, 3749 and 3700 cm^{-1} bands grow and the set IVa bands diminish in intensity (Figs. 27b-c). The spectrum of the sample, evacuated for 43 hours following B^nCl_3 adsorption, exhibits very weak bands at 952 and 922 cm^{-1} and a more intense band at 940 cm^{-1}; the 913 cm^{-1} band has disappeared (Fig. 29c). On adding air, the bands at 952 and 928 cm^{-1} disappear and a strong band at 940 cm^{-1} is produced (Fig. 29d). The 940 cm^{-1} band is replaced by a band at 880 cm^{-1} with the simultaneous replacement of the set IVa and set Va bands by set VIa bands (Fig. 27e) on exposing the sample to air for 24 hours (Fig. 29e).

B^nCl_3 adsorbed on silica samples evacuated at 1020°C

Figure 30a shows the spectrum of a silica sample to which 0.6 cm B^nCl_3 was added for 45 minutes followed by 1 min. evacuation. The silica disc, which had been evacuated at 1020°C for 8 hours prior to B^nCl_3 adsorption, exhibits a very weak 3749 cm^{-1} (O.D. 0.02) band in the background spectrum. A band at 1365 cm^{-1} and a weaker band at 1395 cm^{-1} (set IVb) are present in figure 30a. On 13 hours evacuation, the set IVb bands have decreased and weak shoulders at 1458, 1428 and 1410 cm^{-1} are produced (Fig. 30b). After 34 hours evacuation, the set IVb bands have disappeared and three strong bands at 1458, 1428 and 1410 cm^{-1} and four weaker bands at

1500, 1480, 1470 and 1325 cm^{-1} are present (Fig. 30c). On evacuating the sample for 59 hours, both the 1410 and 1428 cm^{-1} band intensities have increased of which the 1428 cm^{-1} is weaker than the 1410 cm^{-1} band (Fig. 30d). The 1458, 1470 and 1480 cm^{-1} bands are present as weak shoulders and the 1500 cm^{-1} band has disappeared. After 83 hours evacuation, a sharp band at 1410 cm^{-1} and very weak shoulders at 1428, 1470 and 1480 cm^{-1} are observed; the remaining bands in set Vb are absent (Fig. 30e). The intensity of the 1325 cm^{-1} band has increased slightly during evacuation. On adding air to the sample, the 1410 cm^{-1} band intensity decreases and two bands at 1420 and 1375 and a weaker band at 1475 cm^{-1} are produced (Fig. 30f) (set VIb). On exposing the sample to air for 24 hours, the remaining set Vb bands are replaced by the set VIb bands which have the same frequencies as the set VIa bands (Fig. 27e).

The spectral behaviour of the bands observed in the 3800-3600 cm^{-1} region is shown in figures 31a-g. On adding B^nCl_3 to the silica sample, the intensity of the weak 3749 cm^{-1} band (O.D. 0.02) present in the background spectrum (Fig. 31a) does not change (Fig. 31b). After evacuating the sample for 13 hours, following B^nCl_3 adsorption, an additional band at 3700 cm^{-1} (O.D. 0.05) is produced (Fig. 31c). On subsequent evacuation, the intensity of the 3700 cm^{-1} band increases but that of the 3749 cm^{-1} band remains unchanged. After degassing the sample for 37 and 89 hours, the 3700 cm^{-1} band intensity increases to O.D. 0.15 and 0.2 respectively

(Figs. 31d-e). The 3700 cm^{-1} band appears at the same time as the set Vb bands are first observed (Fig. 30b) and its growth parallels that of the set Vb bands (Figs. 30c-d). In other experiments, a very small increase in the 3749 cm^{-1} band intensity was sometimes observed. On adding air to the sample, the intensity of the 3700 cm^{-1} band does not change and the 3749 cm^{-1} band intensity increases to O.D. 0.07 (Fig. 31g). On exposing the sample to air for 24 hours, the 3749 cm^{-1} band has grown to O.D. 0.09 and the 3700 cm^{-1} band has decreased to O.D. 0.16 (Fig. 31f).

The corresponding spectra in the 1000-800 cm^{-1} region are given in figures 32a-g. On adsorbing B^nCl_3 to the sample, the 908 and 890 cm^{-1} bands in the background spectra (Fig. 32a) are replaced by a strong band at 913 cm^{-1} and a weaker band at 952 cm^{-1} (Fig. 32b). The intensity of the 952 cm^{-1} band exhibited by a low temperature heated silica surfaces (Fig. 29a) was always greater than the intensity of the same band produced on high temperature heated silica surfaces (Fig. 32b). On evacuation, the 952 and 913 cm^{-1} band intensities gradually decrease (Fig. 32c) and both bands disappear after 37 hours evacuation (Fig. 32d). The spectrum of the sample evacuated for 87 hours following B^nCl_3 adsorption exhibits a weak shoulder at 940 cm^{-1} (Fig. 32e). On adding air to the cell, the 940 cm^{-1} band increases in intensity (Fig. 32f) but is completely replaced by a band at 880 cm^{-1} on greater contact with air (Fig. 32g).

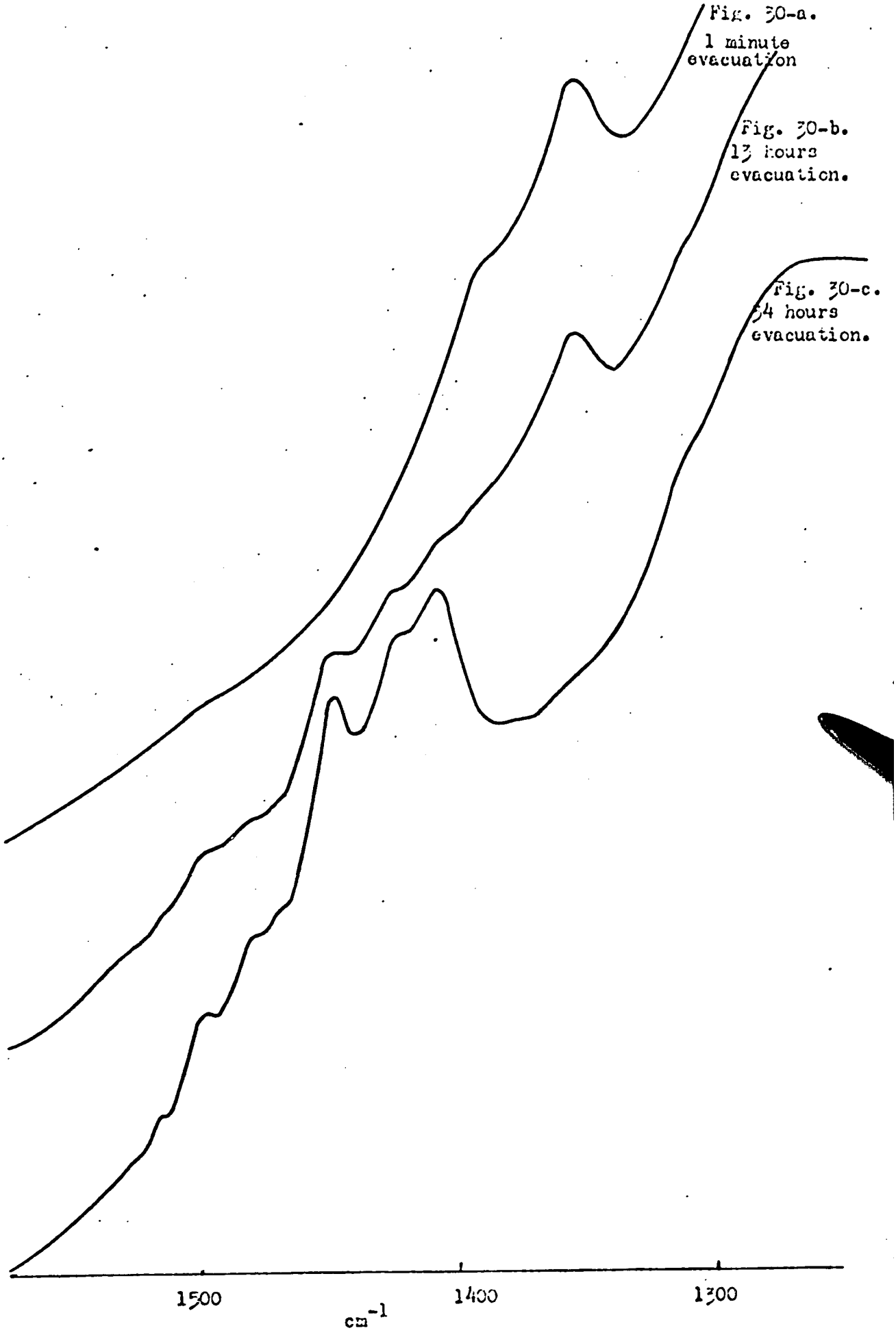


Figure 30. 0.6 cm. $B^{n}Cl_3$ adsorbed on silica.

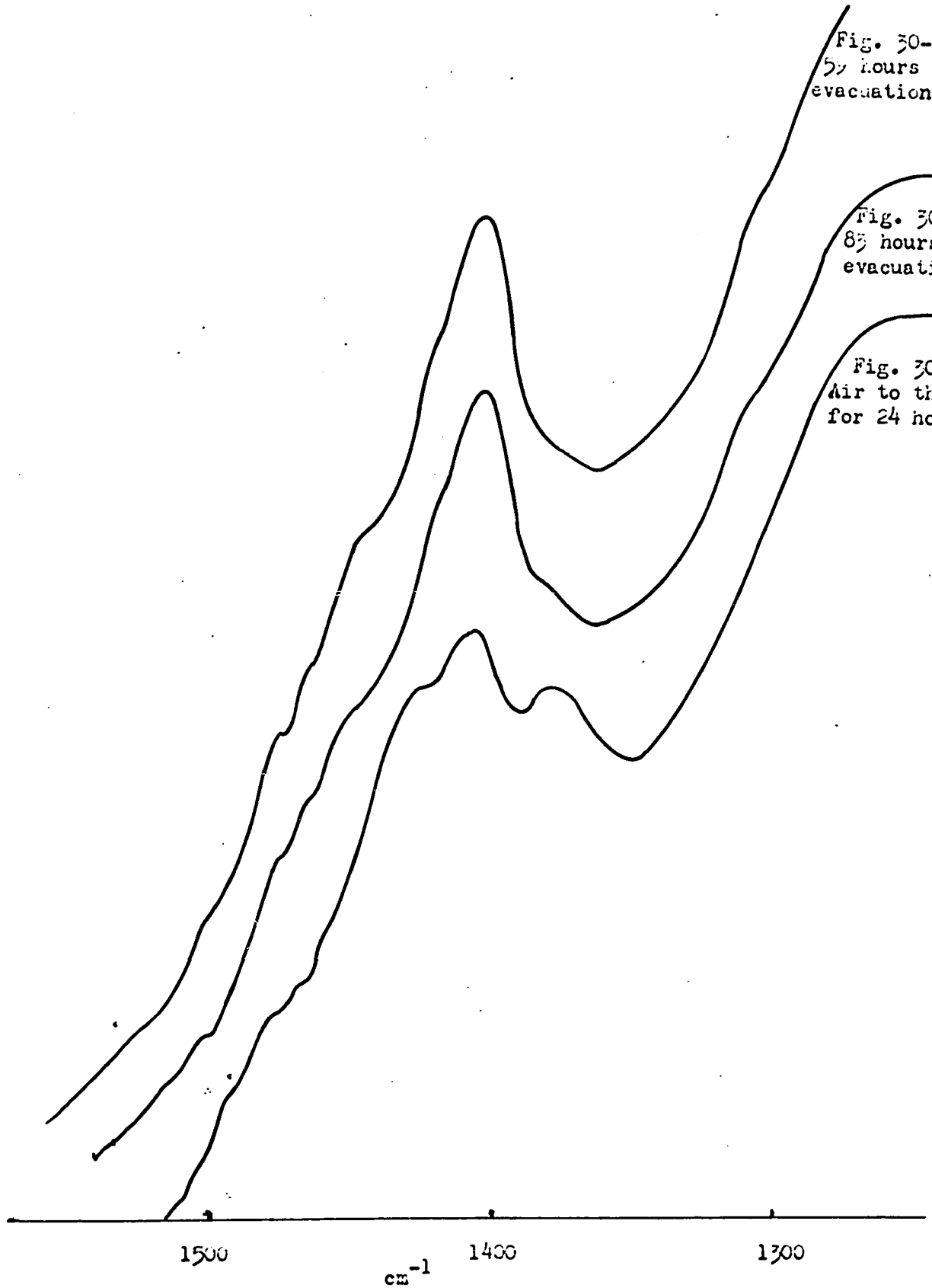


Fig. 30-d.
5½ hours
evacuation.

Fig. 30-e.
8½ hours
evacuation.

Fig. 30-f.
Air to the cell
for 24 hours.

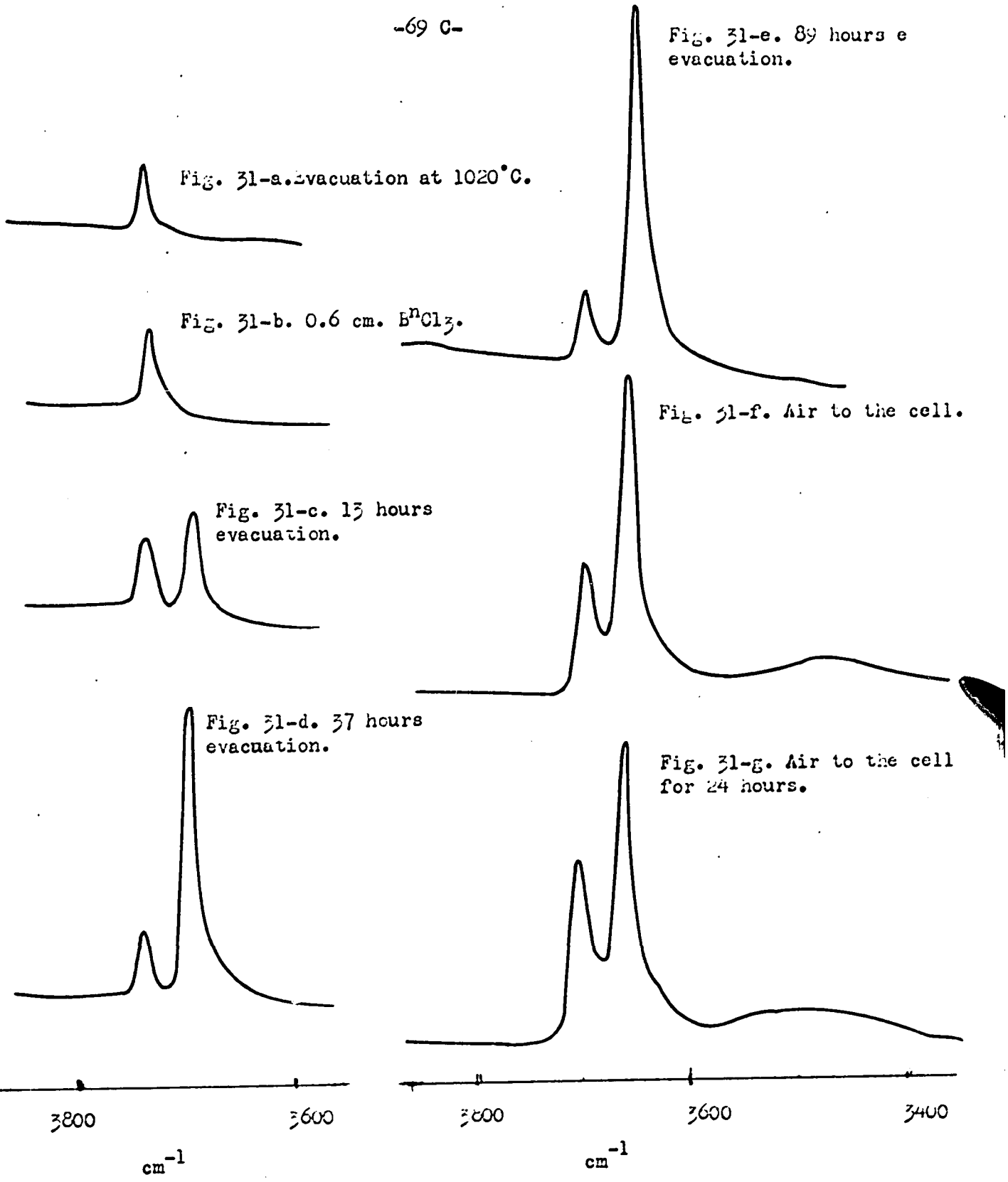


Figure 31. 0.6 cm. B^nCl_3 adsorbed on silica.

Fig. 32-a. Evacuation at 1020°C.

Fig. 32-b. 0.6 cm. B^nCl_3.

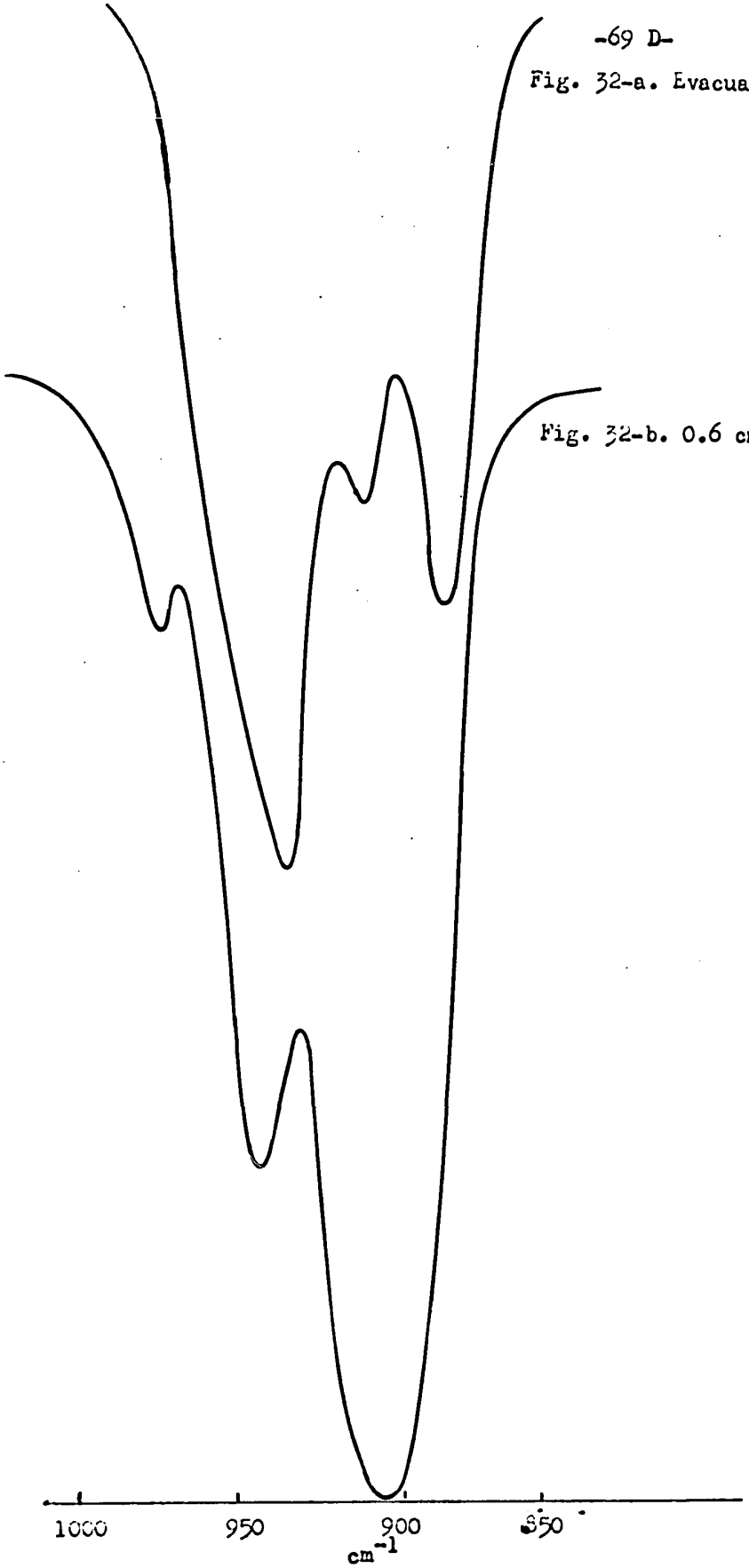


Figure 32. 0.6 cm. B^nCl_3 adsorbed on silica.

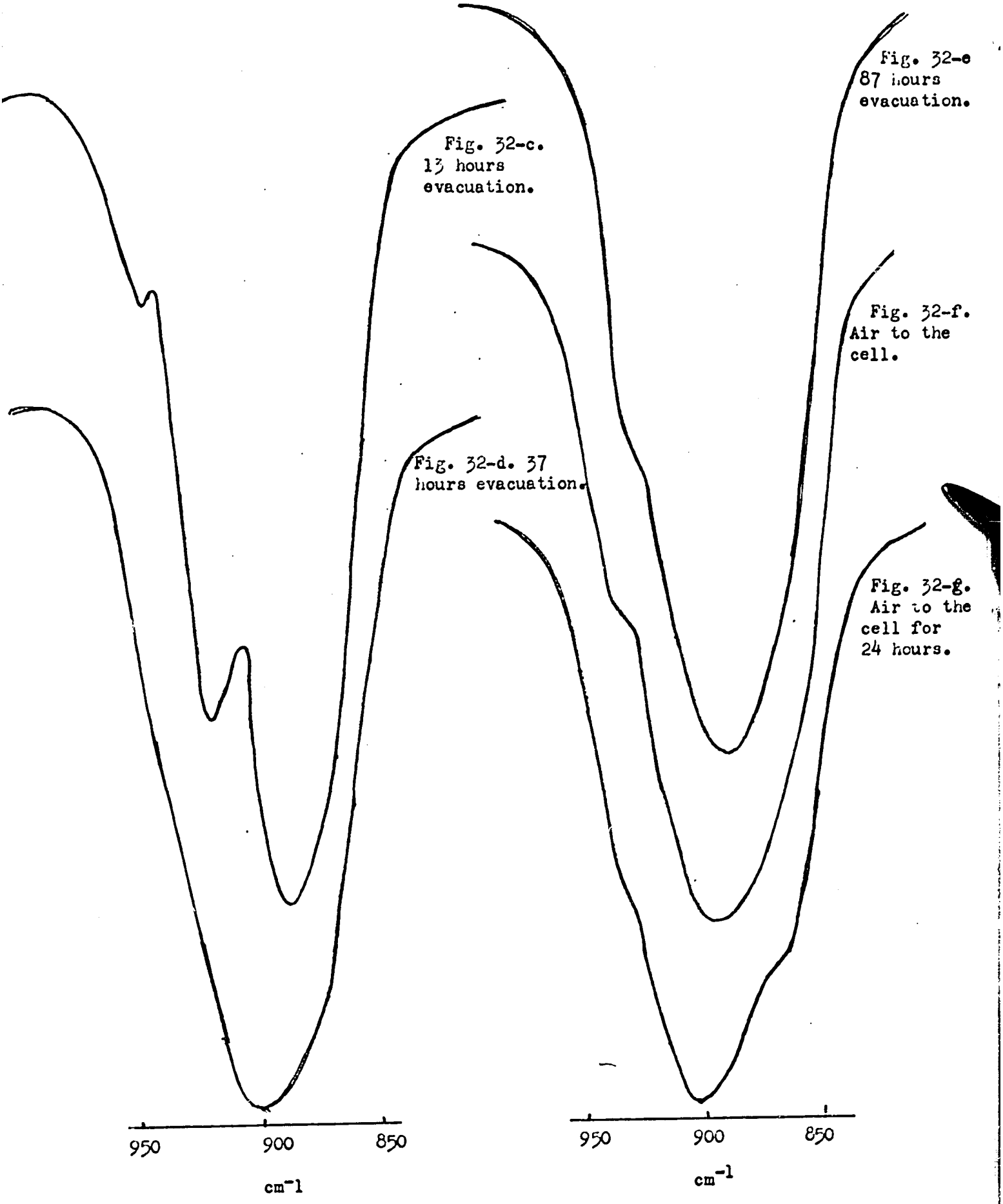


Fig. 32-c. 13 hours evacuation.

Fig. 32-d. 37 hours evacuation.

Fig. 32-e 87 hours evacuation.

Fig. 32-f. Air to the cell.

Fig. 32-g. Air to the cell for 24 hours.

$B^{10}Cl_3$ adsorbed on silica

Figure 33a shows the spectrum of a silica sample to which 0.7 cm $B^{10}Cl_3$ was added for 15 seconds followed by 1 minute evacuation. The sample was evacuated at 900°C for 6 hours prior to $B^{10}Cl_3$ adsorption. A band at 1395 cm^{-1} (set IVc), more intense than the 1395 cm^{-1} band in set IVa (Fig. 29a) is produced on adding $B^{10}Cl_3$. After 14 hours evacuation, the intensity of the 1395 cm^{-1} band decreases and a broad unresolved band (set Vc) is produced (Fig. 33b). On 47 hours evacuation, a greatly diminished 1395 cm^{-1} band and a stronger set Vc band that contains three peaks at 1480, 1470 and 1435 cm^{-1} are observed (Fig. 33d). On adding air to the cell for 24 hours, the set Vc and the remaining set IVc bands are replaced by two bands at 1475 and 1425 cm^{-1} (set VIc) (Fig. 33f).

The background spectrum of this silica which had been evacuated at 900 C exhibits a strong 3749 cm^{-1} band (O.D. 0.4) (Fig. 34a). On adsorbing 0.7 cm $B^{10}Cl_3$, the 3749 cm^{-1} band is reduced to O.D. 0.07 (Fig. 34b). After evacuating the sample for 14 hours following $B^{10}Cl_3$ adsorption, the intensity of the 3749 cm^{-1} band is unchanged and an additional band at 3700 cm^{-1} (O.D. 0.06) is produced (Fig. 34c). On subsequent evacuation, both the 3749 and 3700 cm^{-1} band continue to grow (Fig. 34d) so that after 47 hours evacuation, the 3749 and 3700 cm^{-1} band intensities have increased to O.D. 0.25 and 0.1 respectively (Fig. 34e). On adding air to the sample

following 44 hours evacuation, the intensities of these two bands increase to O.D. 0.32; an additional strong broad band at 3230 cm^{-1} is also produced (Fig. 34f). The spectrum after 24 hours contact with air, exhibits a stronger 3749 cm^{-1} band (O.D. 0.4) and a weaker 3700 cm^{-1} band (O.D. 0.2) together with a strong 3230 cm^{-1} band (Fig. 34g). It is seen from figures 33 and 34 that the growth of the 3749 and 3700 cm^{-1} bands parallels the growth of the set Vc and the removal of the set IVc bands on evacuation.

On adsorbing 0.7 cm $B^{10}Cl_3$ to this sample, a band at 933 cm^{-1} (Fig. 35a) together with the set IVc bands (Fig. 31a) is produced. On subsequent evacuation, the intensity of the 933 cm^{-1} band decreases; however, the band becomes wider and shifts slightly to higher frequency (Figs. 35b-e). After 44 hours evacuation, a sharp band at 940 cm^{-1} is present together with a very weak shoulder at 933 cm^{-1} (Fig. 35e). On adding air, the weak 933 cm^{-1} band is removed and a strong 940 cm^{-1} band together with a weaker 880 cm^{-1} is observed (Fig. 35f). On exposing the sample to air for 16 hours, the 940 cm^{-1} band is completely replaced by a stronger band at 880 cm^{-1} (Fig. 35g).

$B^{10}Cl_3$ adsorbed on silica samples evacuated at 1010°C

The spectrum in the 3800-3600 region of a silica sample, evacuated at 1010°C for 5 hours exhibits a weak band at 3749 cm^{-1} (Fig. 37a). On adding 0.9 mm $B^{10}Cl_3$ for 15 seconds

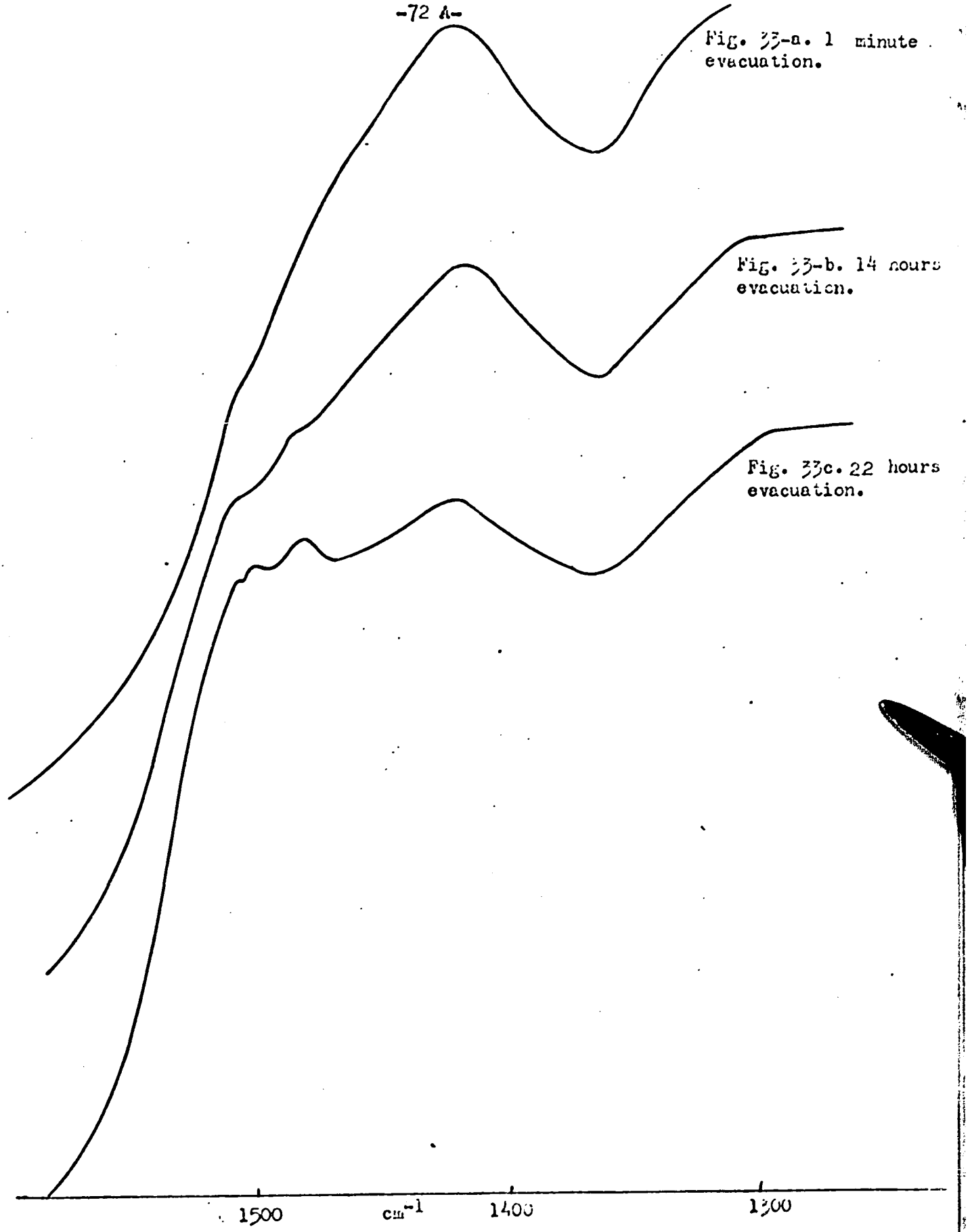


Figure 33. 0.7 cm. $B^{10}Cl_3$ adsorbed on silica.

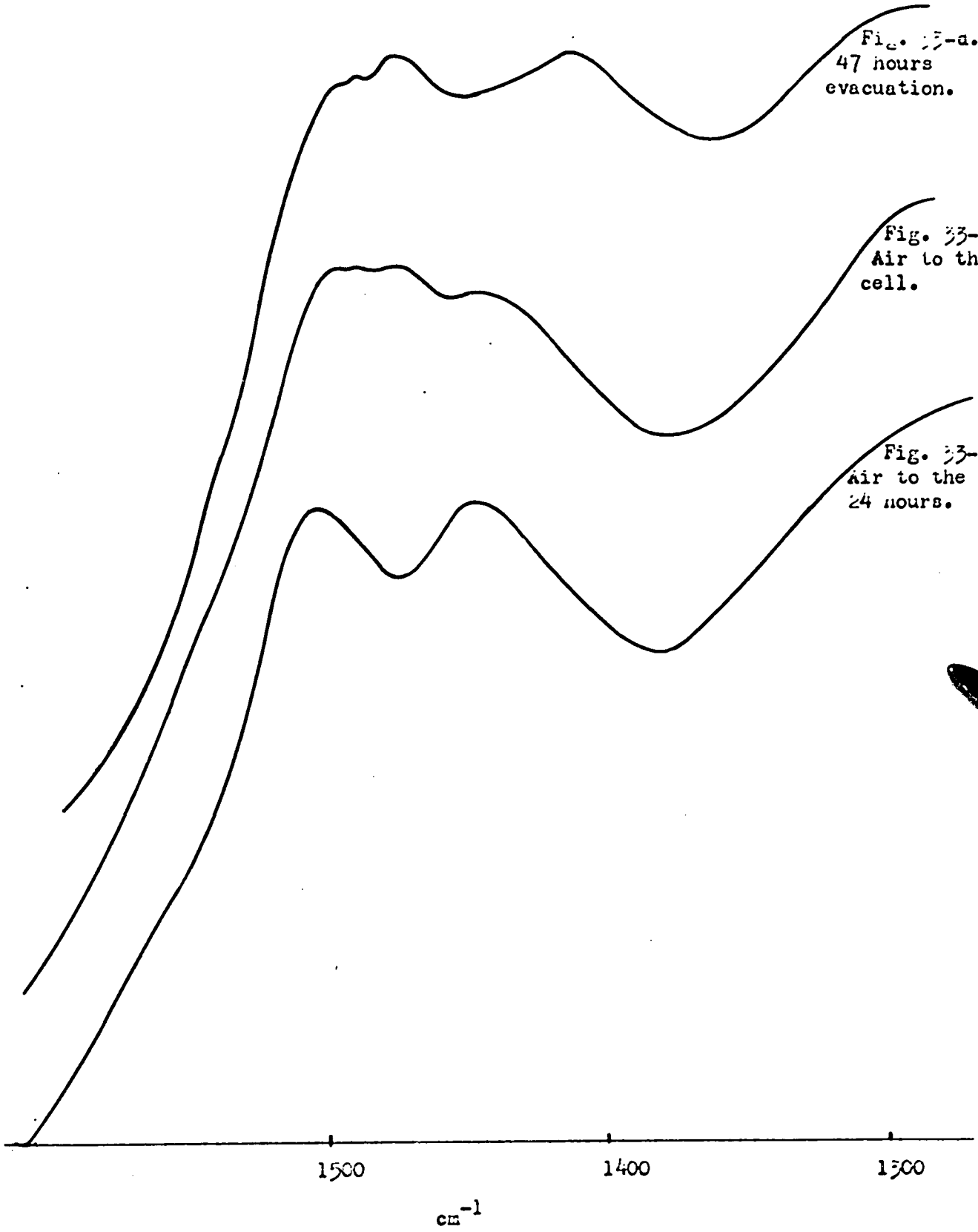


Fig. 33-a.
47 hours
evacuation.
Fig. 33-e.
Air to the
cell.
Fig. 33-f.
Air to the cell
24 hours.
1500
1400
1300
cm-1

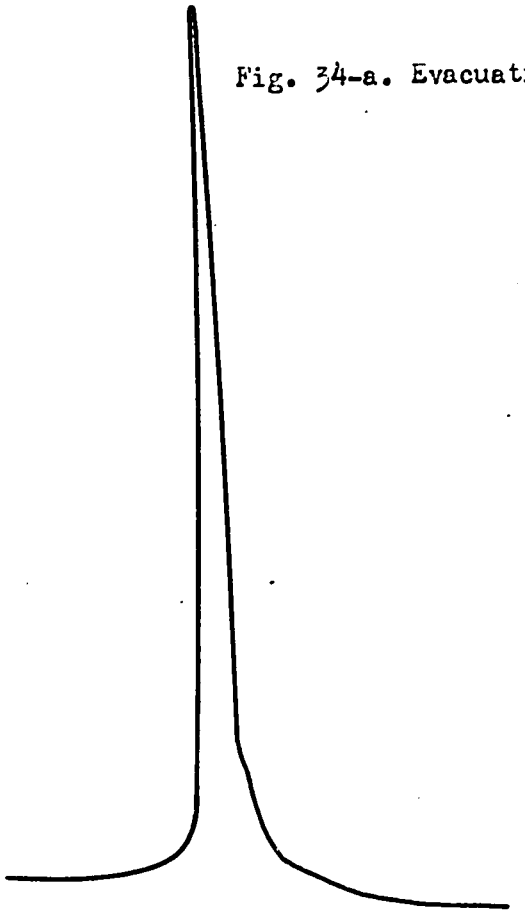


Fig. 34-a. Evacuation at 900°C.

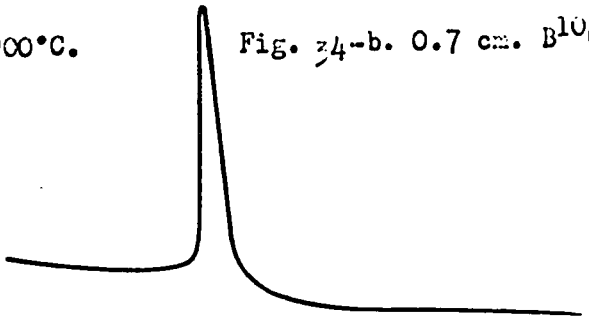


Fig. 34-b. 0.7 cm. $B^{10}Cl_3$.

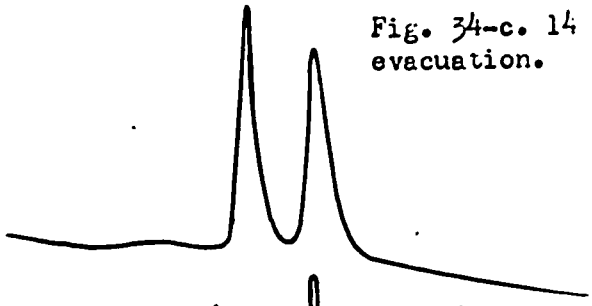


Fig. 34-c. 14 hours evacuation.

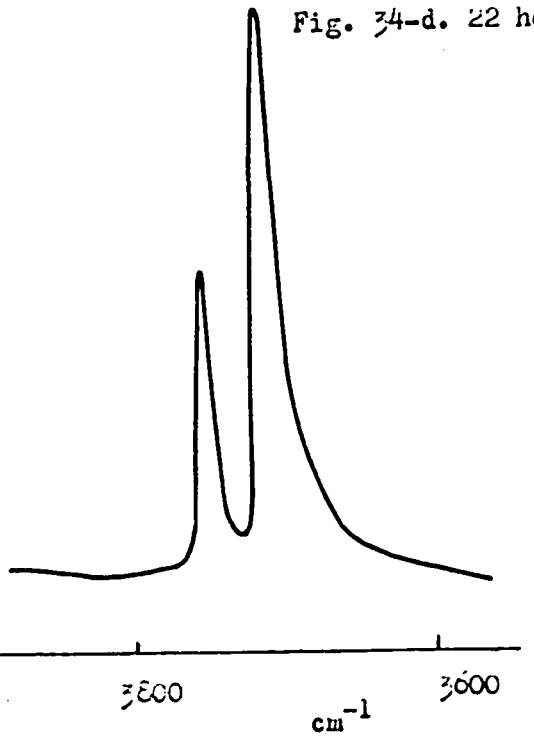


Fig. 34-d. 22 hours evacuation.

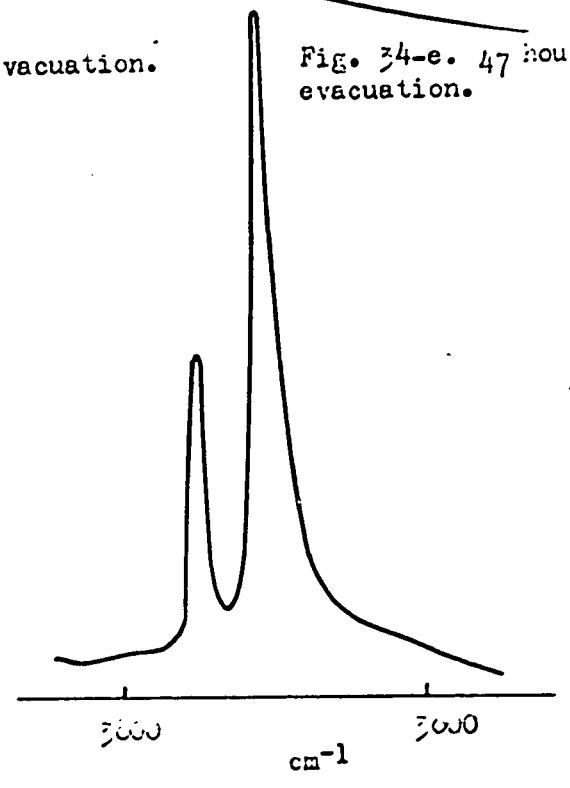


Fig. 34-e. 47 hours evacuation.

Figure 34. 0.7 cm. $B^{10}Cl_3$ adsorbed on silica.

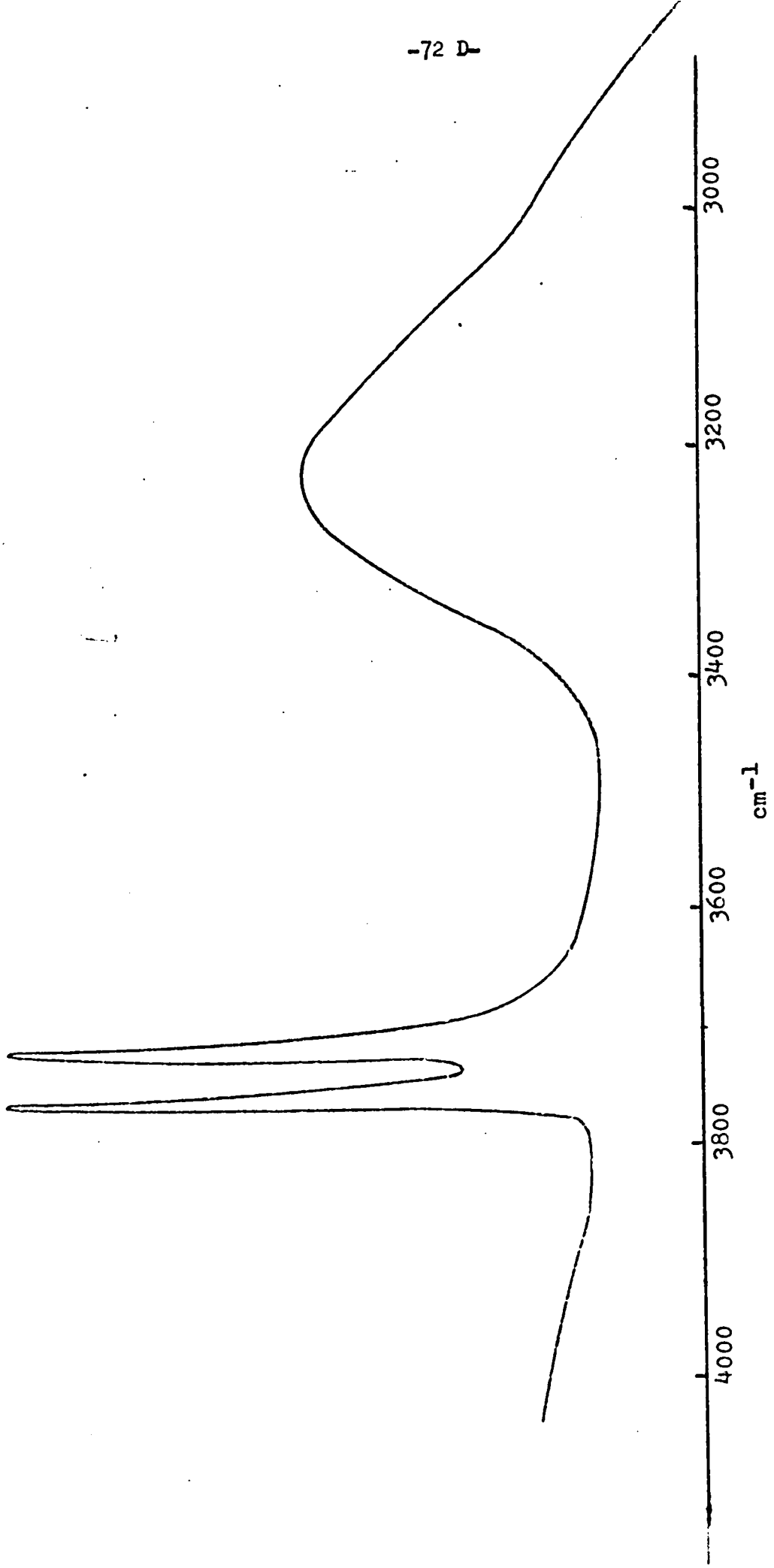


Fig. 34f Air to the cell

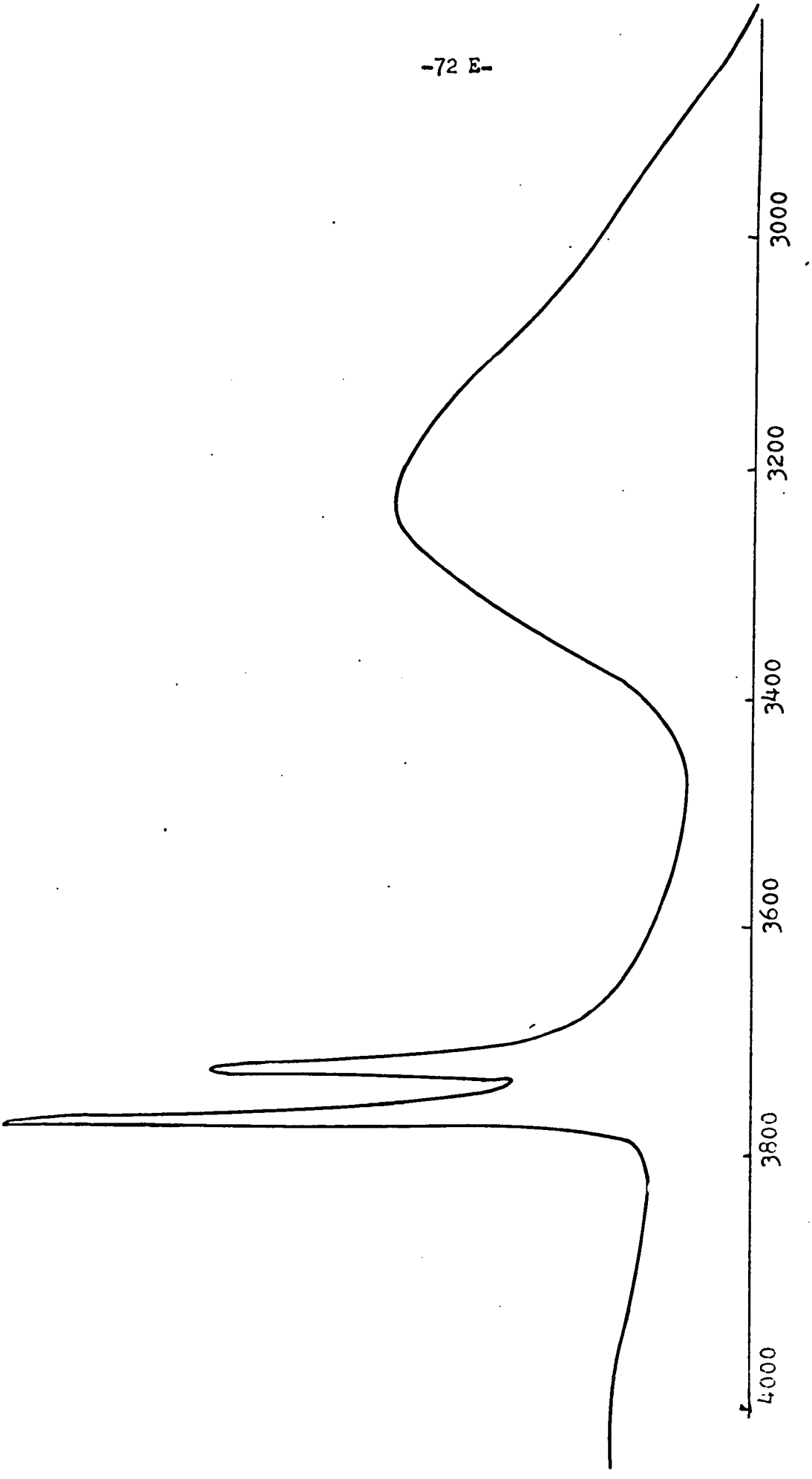


Fig. 34r Air to the cell for 24 hours

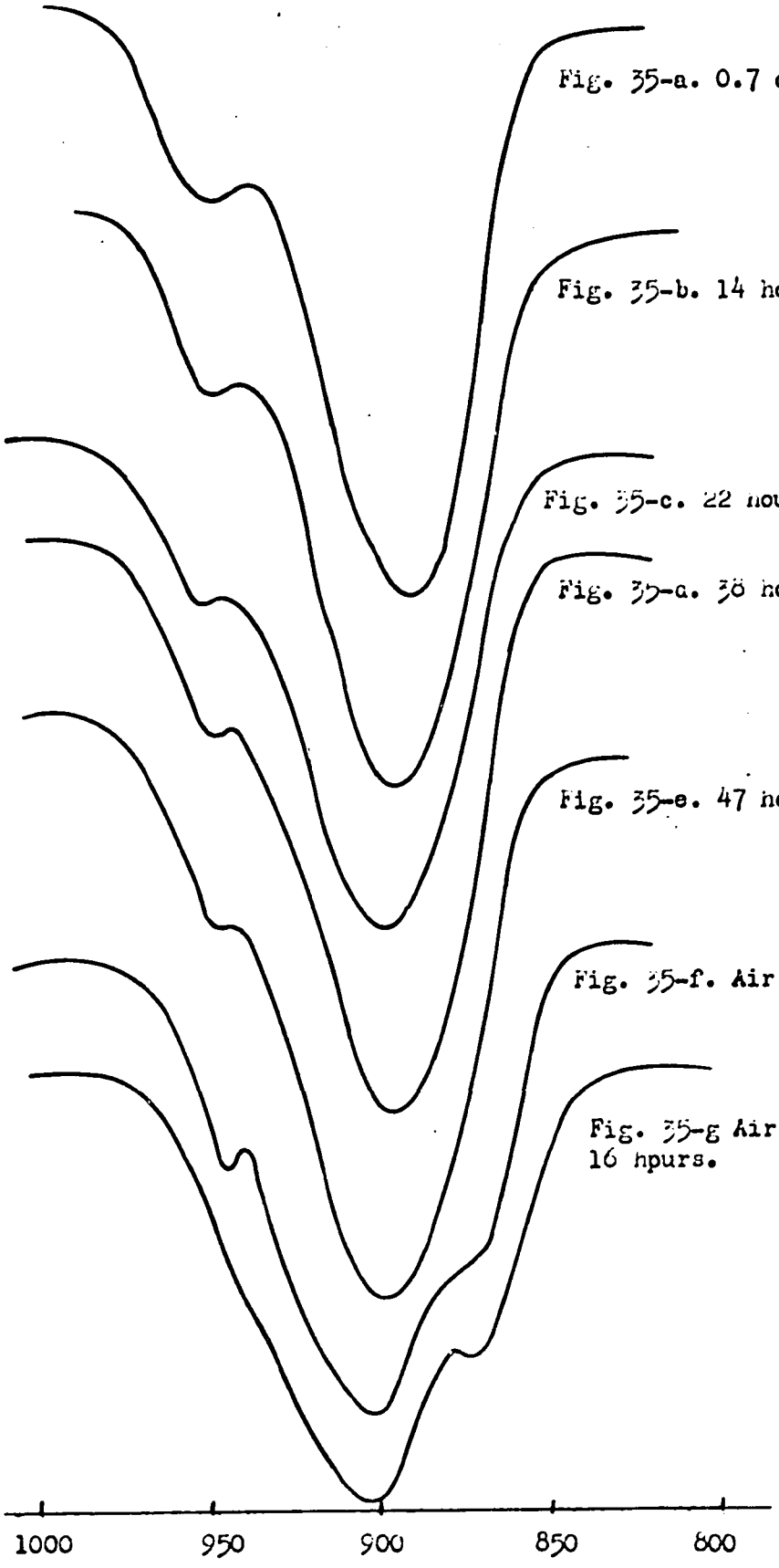


Figure 35. 0.7 cm. $B^{10}Cl_3$ adsorbed on silica.

followed by 1 minute evacuation, a strong sharp band at 1395 cm^{-1} (set IVd) is produced (Fig. 36a) (set Vd). On evacuating the sample for 16 hours following $B^{10}Cl_3$ adsorption, the intensity of the 1395 cm^{-1} band is diminished and four new bands at 1500, 1480, 1470 and 1455 cm^{-1} together with a weaker band at 1365 cm^{-1} are produced (Fig. 36b). On 40 hours evacuation, the 1470, 1455 and 1365 cm^{-1} band intensities have increased and the 1500 and 1395 cm^{-1} bands have disappeared; the 1480 cm^{-1} band is present as a weak shoulder (Fig. 36c). On adding air, shoulders at 1475 and 1425 cm^{-1} are produced (Fig. 36d) and on longer contact with air, the set Vd bands are replaced by two bands at 1475 and 1425 cm^{-1} (set VId).

On adding 0.9 mm $B^{10}Cl_3$, the intensity of the weak (O.D. 0.03) 3749 cm^{-1} band (Fig. 37a) present in the background spectrum does not change (Fig. 37b). After 16 hours evacuation, an additional band at 3700 cm^{-1} (O.D. 0.07) is observed. On 44 hours evacuation, following $B^{10}Cl_3$ adsorption, the 3749 and 3700 cm^{-1} bands have grown to O.D. 0.04 and 0.17 respectively (Fig. 37d). On adding air to the cell, the 3749 cm^{-1} band has grown to O.D. 0.06 and the intensity of the 3700 cm^{-1} band has not changed (Fig. 37e). The spectrum of the sample, on 16 hours contact with air, exhibits a stronger 3749 cm^{-1} band (O.D. 0.08) and a diminished 3700 cm^{-1} (O.D. 0.14) band (Fig. 37g).

The spectra of the corresponding bands observed in the 1000-800 cm^{-1} region are given in figures 38a-f. On adsorbing

$B^{10}Cl_3$ to the silica sample, the characteristic bands at 908 and 890 cm^{-1} present in the background spectrum (Fig. 38a) are replaced by a strong band at 922 cm^{-1} (Fig. 38b). On further evacuation, the intensity of the 922 cm^{-1} band decreases with the lowering of the set IVd bands (Fig. 38c). After 40 hours evacuation, when the set IVd bands have been removed and a strong set Vd bands are present in the corresponding spectrum of the 1650-1300 cm^{-1} region (Fig. 36c), the 922 cm^{-1} band is completely replaced by a weak shoulder at 940 cm^{-1} (Fig. 38d). On adding air to the cell, the intensity of tne 940 cm^{-1} band is increased and a weak 880 cm^{-1} band is present (Fig. 38e). On exposing the sample to air for 24 hours, the 940 cm^{-1} band is replaced by a stronger band at 880 cm^{-1} (Fig. 38f).

The frequencies of the bands produced in the 1650-1300 cm^{-1} region and the number of their corresponding sets are listed in table 6. Since the spectral behaviour of the bands in the same subsets are found to be similar under various experimental conditions, all the bands in each subset will be referred to by their set numbers only, i.e. the sets IVa, IVb, IVc and IVd will be termed at set IV only etc.

A list of the bands produced in the 1000-800 cm^{-1} region in the spectra of silica samples on BCl_3 adsorption (a), subsequent evacuation (B) and reaction with air (C) is given in Table 7.

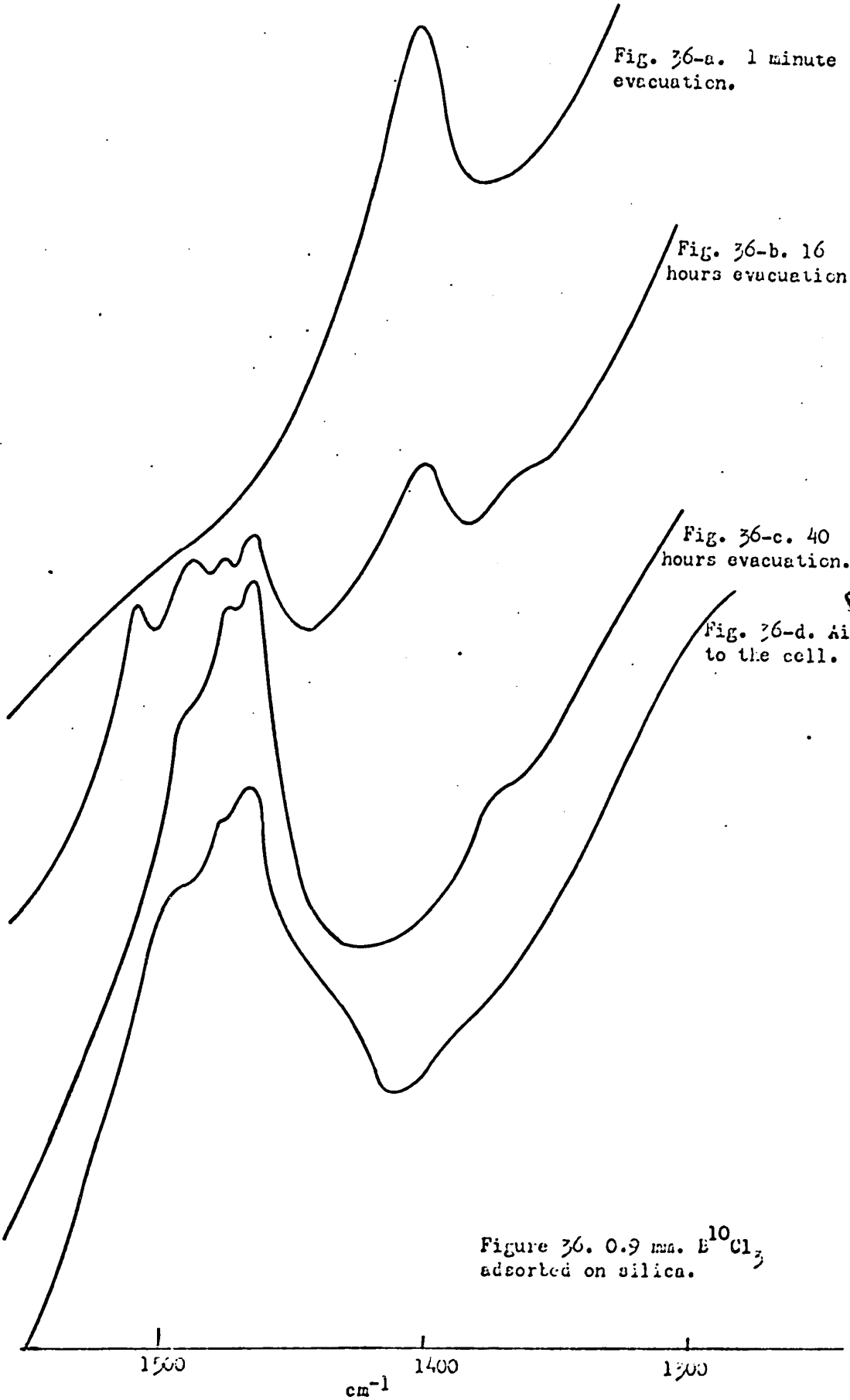


Figure 36. 0.9 mm. $B^{10}Cl_3$ adsorbed on silica.

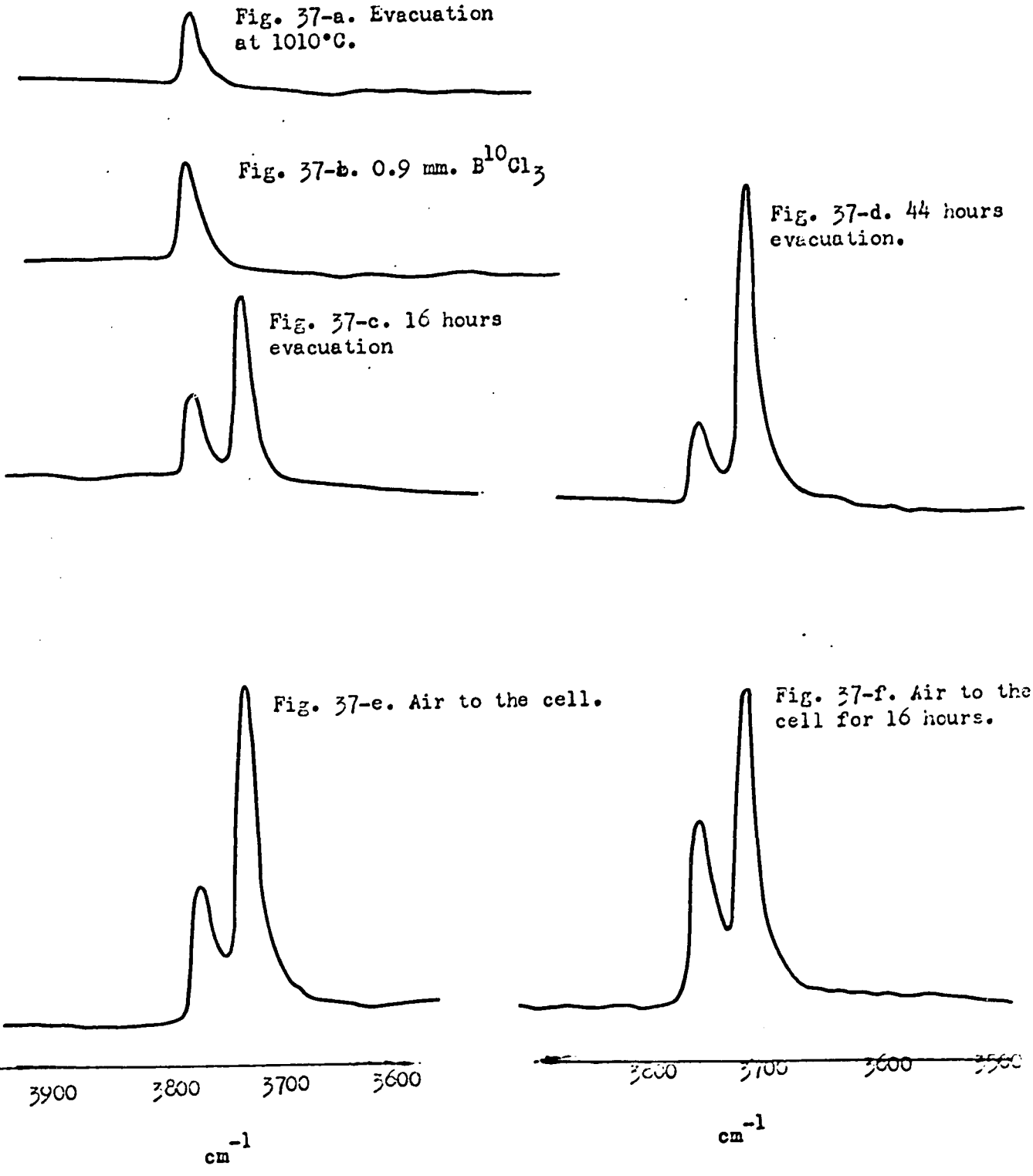


Figure 37. 0.9 mm. $B^{10}Cl_3$ adsorbed on silica.

Fig. 38-a. Evacuation at 1010°C.

Fig. 38-b. 0.9mm. $B^{10}Cl_3$.

Fig. 38-c. 16 hours evacuation

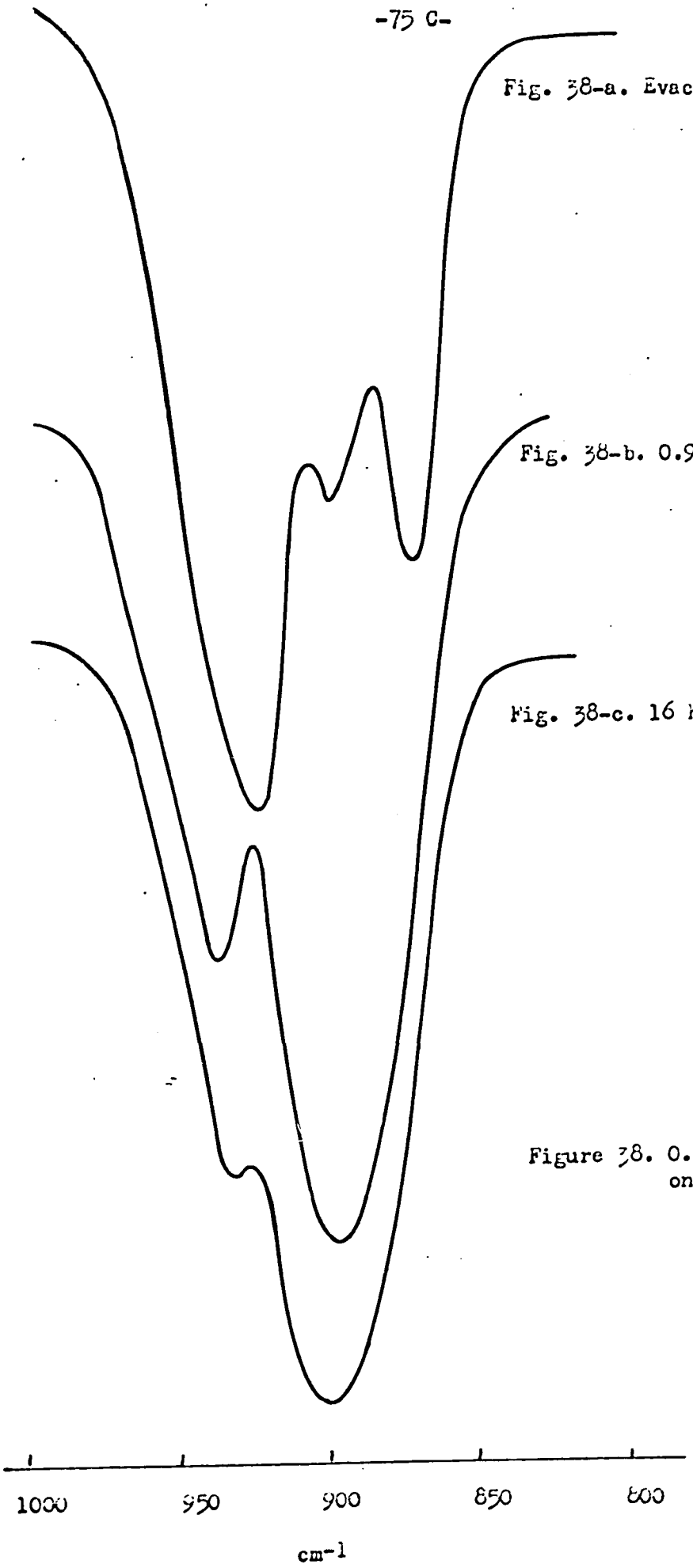


Figure 38. 0.9 mm. $B^{10}Cl_3$ adsorbed on silica.

Fig. 38-d. 40 hours evacuation.

Fig. 38-e. Air to the cell.

Fig. 38-f. Air to the cell 24 hours.

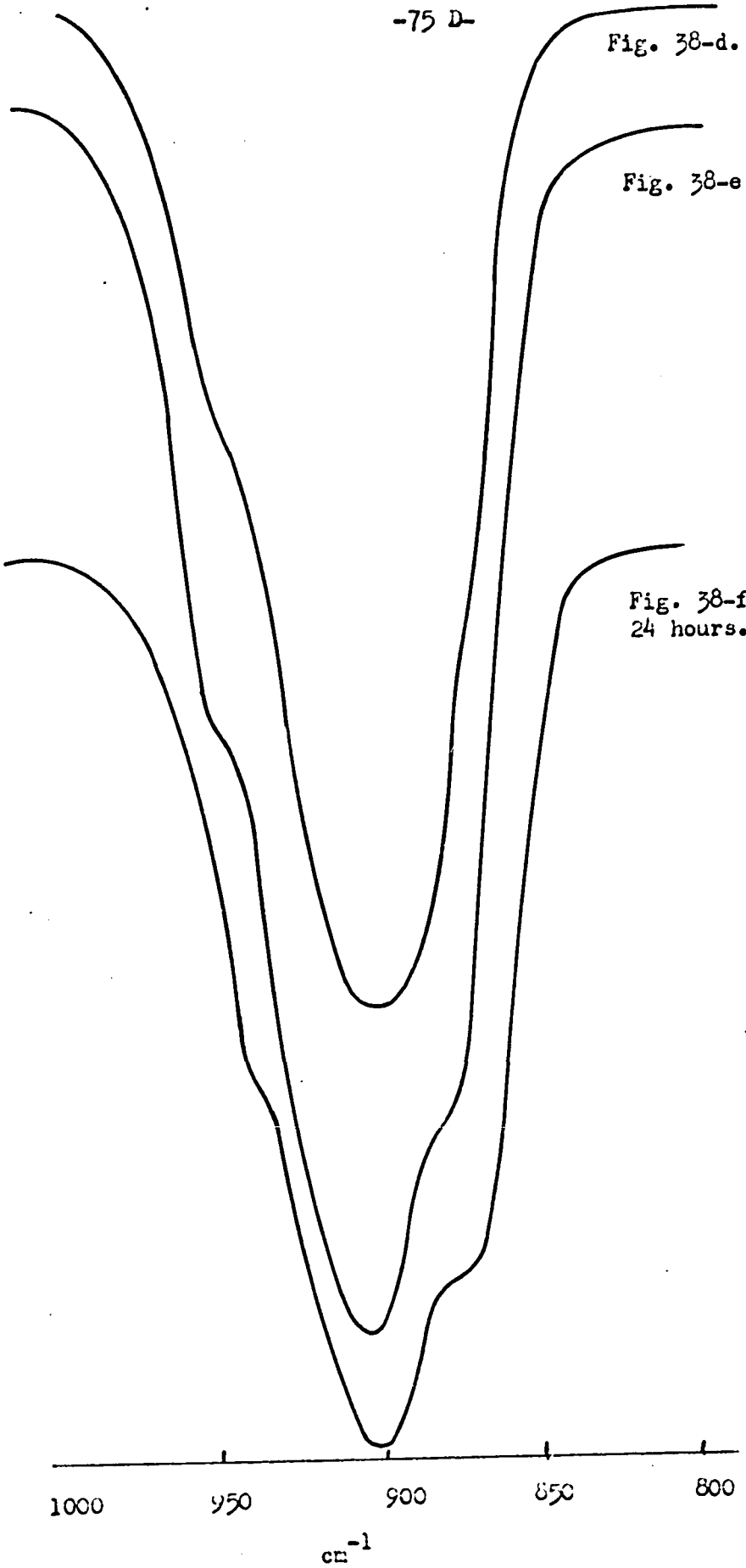


TABLE 6

Adsorbate	Set No.	Frequencies, cm^{-1}
B^nCl_3	IVa	1395, 1365
	Va	1325, a broad band with peaks at 1410, 1428, 1455 and 1470
	VIa	1475, 1420, 1375
B^nCl_3	IVb	1395, 1365
	Vb	1500, 1450, 1470; 1458, 1428, 1410, 1325
	VIb	1475, 1420, 1375
B^nCl_3	IVc	1395
	Vc	1365, a broad band with peaks at 1500, 1470 and 1455 cm^{-1}
	VIc	1475, 1425
B^nCl_3	IVd	1395
	Vd	1500, 1480, 1470, 1455 1365
	VId	1475, 1425

TABLE 7

Adsorbate	T*	A	B	C
$B^{n}Cl_3$	800	952, 928	940	880
	1020	952, 913	940	880
$B^{10}Cl_3$	940 C	933	940	880
	1010	922	940	880

T* = the temperature in °C at which the samples were evacuated prior to adsorption.

The variation in the 3749 cm^{-1} and 3700 cm^{-1} band intensities observed in the spectra of two silica samples, evacuated at 800°C and 1020°C before BCl_3 adsorption, are given in figures 39a and 39b respectively. The maximum intensity (O.D. 0.27) of the 3700 cm^{-1} band in figure 39a is seen to be greater than that in figure 39b (O.D. 0.17); a further distinction is that the intensity of the 3749 cm^{-1} band observed on adding air to the cell, is greater than the corresponding diminished 3700 cm^{-1} band. It is observed from figure 39b that although the 3749 cm^{-1} band has increased on adding air, it is still weaker than the accompanying 3700 cm^{-1} band.

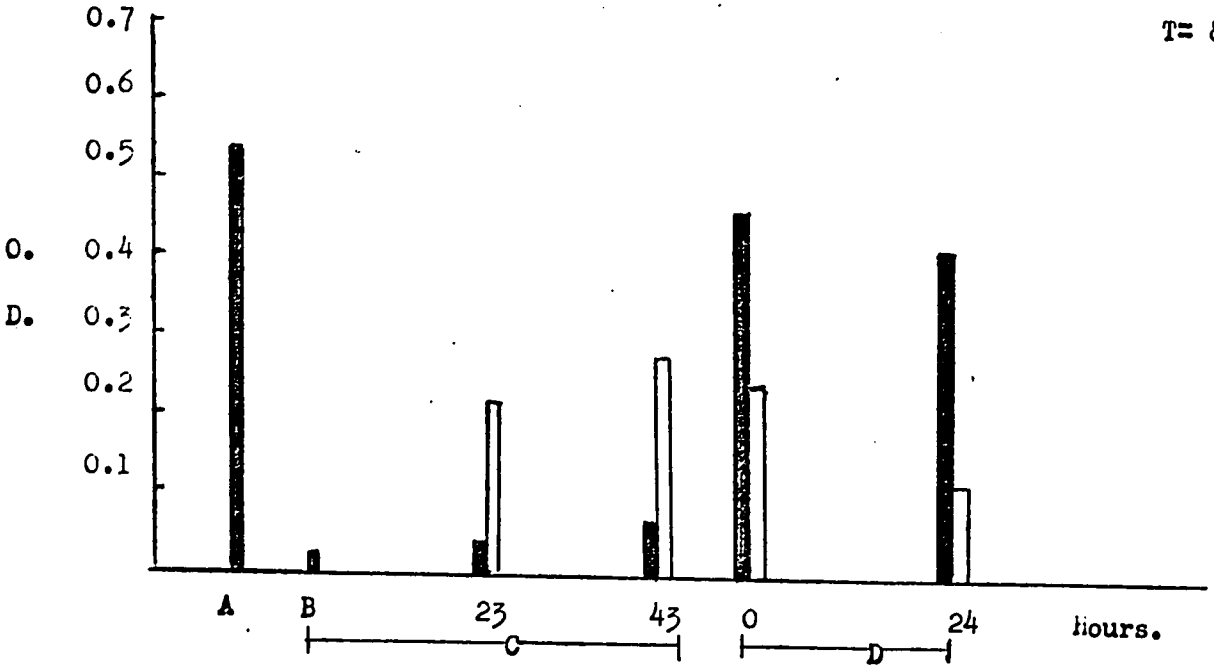


Fig. 39-a. 0.7 cm. $B^{10}Cl_3$ adsorbed on silica.

T = Temperature of dehydration.

A = Initial intensity.

B = BCl_3 adsorption .

C = Evacuation period (hours) .

D = Reaction time with air (hours).

Intensity ofthe SiOH (O-H str.) band.

Intensity of the BOH (O-H str.) band.

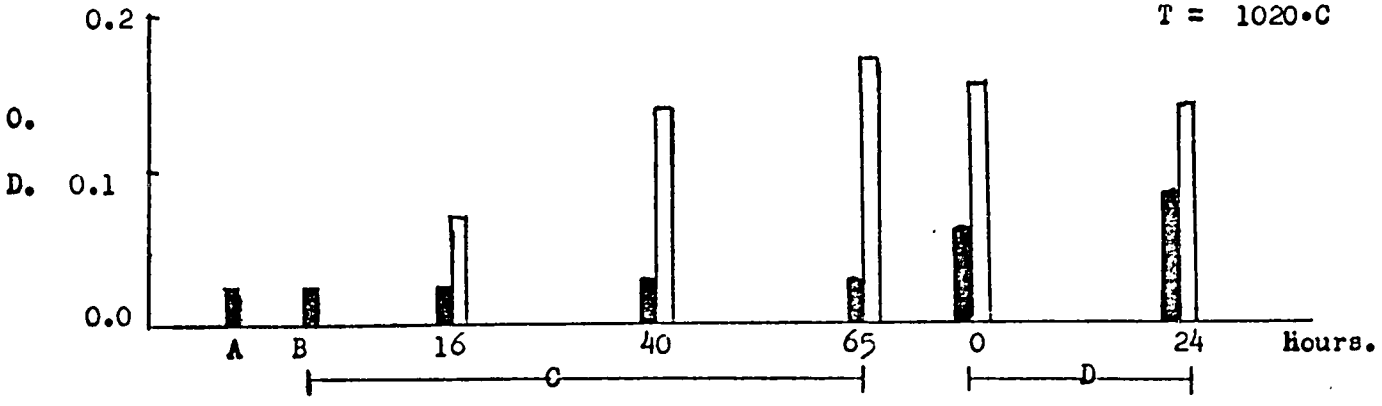


Fig. 39-b. 0.6 cm $B^{11}Cl_3$ adsorbed on silica.

In comparing the spectra of BF_3 and BCl_3 treated silica samples, the following observations can be made:

1) On evacuation, only the characteristic Si-O-H band at 3749 cm^{-1} is produced with BF_3 treated silica; whereas the spectra of BCl_3 treated samples exhibit another band at 3700 cm^{-1} on evacuation.

2) The initial set of bands (Set IV) produced on adsorbing BCl_3 to silica samples evacuated at temperatures above or below 1000°C undergo change on evacuation. The Set I bands observed on adsorbing BF_3 to silica sample evacuated above 1000°C are stable to evacuation but the corresponding bands produced on samples evacuated below 1000°C, are replaced on evacuation.

BCl_3 adsorbed on H_2O^{18} exchanged silica

Figure 40a shows the spectrum of a H_2O^{18} exchanged silica sample to which 0.2 mm $B^{10}Cl_3$ was added. The sample was first evacuated at 800°C, exchanged (60%) with H_2O^{18} at 400°C and then further evacuated at 1010°C for 9 hours. Two bands at 1395 and 1367 cm^{-1} are produced of which the 1395 cm^{-1} band is stronger one and is also produced with unexchanged silica samples. On 28 hours evacuation, the intensities of these bands decrease and a broad band with shoulders at 1490, 1470, 1455, 1440 cm^{-1} appear (Fig. 40b). After 103 hours evacuation, the 1395 and 1367 cm^{-1} bands have disappeared and a strong broad band with peaks at 1490, 1480, 1450 cm^{-1} is present (Fig. 40c). On adding air, a band at 1425 cm^{-1} and a broad band from 1475-1450 cm^{-1} are produced (Fig. 40d).

On adding 0.2 mm B^nCl_3 to a H_2O^{18} exchanged silica two bands at 1365 and 1333 cm^{-1} and a weaker band at 1395 cm^{-1} are produced (Fig. 41a). The sample was evacuated at 800°C following exchange. On evacuation, the intensities of the bands decrease and on adding air, only a broad band from 1420-1350 cm^{-1} is observed (Figs. 41b and 41c). The spectra in the 3800-3600 cm^{-1} region are identical for exchanged silica samples on which either $B^{10}Cl_3$ or B^nCl_3 has been adsorbed so that only one of the examples need be given here. Figure 42a shows the spectrum of a 60% H_2O^{18} exchanged silica sample

evacuated at 800°C for 8 hours following exchange; the bands at 3749 cm^{-1} (O.D. 0.15) and 3738 cm^{-1} (O.D. 0.25) are present. On adding 1.0 mm $B^{10}Cl_3$, these bands are almost removed (Fig. 42b). After 45 hours evacuation, a weak pair of bands at 3700 (O.D. 0.04) and 3690 cm^{-1} (O.D. 0.03) are produced (Fig. 42c) both of which continue to grow on subsequent evacuation (Fig. 42d-e). The growth of these bands parallels the decrease in intensity of the initial set of band, and the growth of the second set of bands in the 1500-1300 cm^{-1} region. After 136 hours evacuation, the 3700 and 3690 cm^{-1} bands have grown to O.D. 0.24 and 0.13 respectively (Fig. 42e). In other similar experiments, a weak growth of the 3749 and 3738 cm^{-1} bands was sometimes observed. On adding air, the intensity of the 3690 cm^{-1} band decreases and a pair of new bands at 3749 and 3738 cm^{-1} are produced (Fig. 42f); there is also a strong broad band at 3230 cm^{-1}. On greater contact with air, the 3690 cm^{-1} band has disappeared, the 3700 cm^{-1} band has decreased in intensity to O.D. 0.1 and the 3749 and 3738 cm^{-1} bands have grown to O.D. 0.13 and 0.18 respectively (Fig. 42g).

Figure 43a shows the spectrum of a silica sample exchanged at 400°C. On evacuating this sample at 1010°C, the 3749 (O.D. 0.33) and 3738 cm^{-1} (O.D. 0.4) bands, present in figure 43a are reduced to O.D. 0.06 and 0.03 respectively (Fig. 43b). On adding 0.2 mm $B^{10}Cl_3$ the band intensities do not change (Fig. 43c) and after 28 hours evacuation, a weak doublet (O.D. 0.02)

is observed at 3700 and 3690 cm^{-1} (Fig. 43d). On subsequent evacuation the 3700 and 3690 cm^{-1} bands continue to grow so that after 103 hours evacuation, they have increased to O.D. 0.13 and 0.09 respectively (Figs. 43e-f). On adding air, the 3700 cm^{-1} band intensity increases to O.D. 0.17, the 3749 and 3738 to O.D. 0.06 and the 3690 cm^{-1} band intensity has decreased (Fig. 43g). On 59 hours contact with air, the 3749 and 3738 cm^{-1} doublet has grown to O.D. 0.11, the 3700 cm^{-1} band has lowered to O.D. 0.15 and the 3690 cm^{-1} band has appeared (Fig. 43h).

The spectra in the 1000-800 cm^{-1} frequency region of the H_2O^{18} exchanged silica samples to which either $B^{10}Cl_3$ or $B^{n}Cl_3$ has been added are identical to the corresponding spectra of the unexchanged silica samples (Table 7).

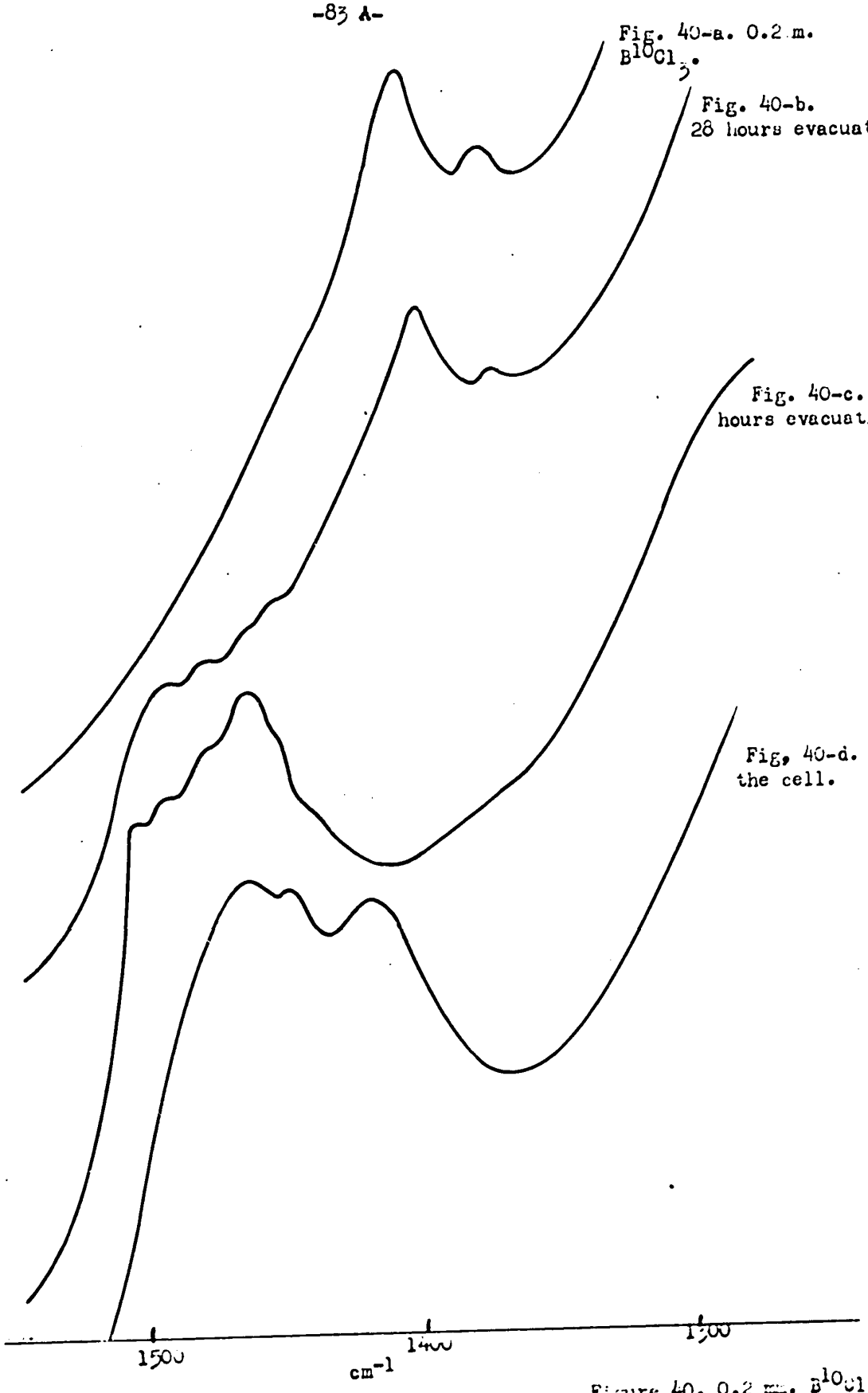


Figure 40. 0.2 m. $B^{10}Cl_3$ adsorbed on H_2O^{10} exchanged silica.

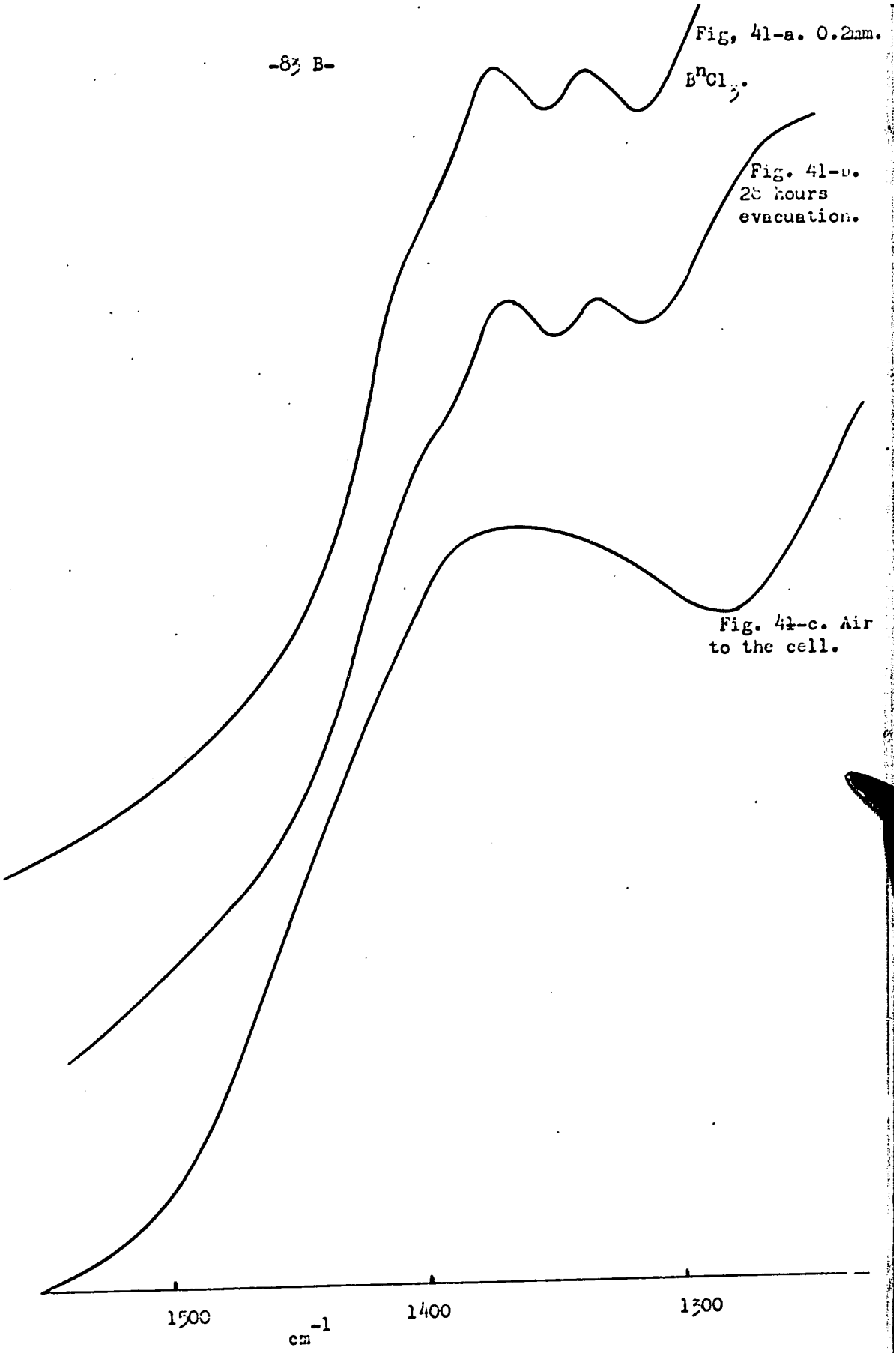


Figure 41. 0.2 mm. B^nCl_3 adsorbed on H_2O^{18} exchanged silica.

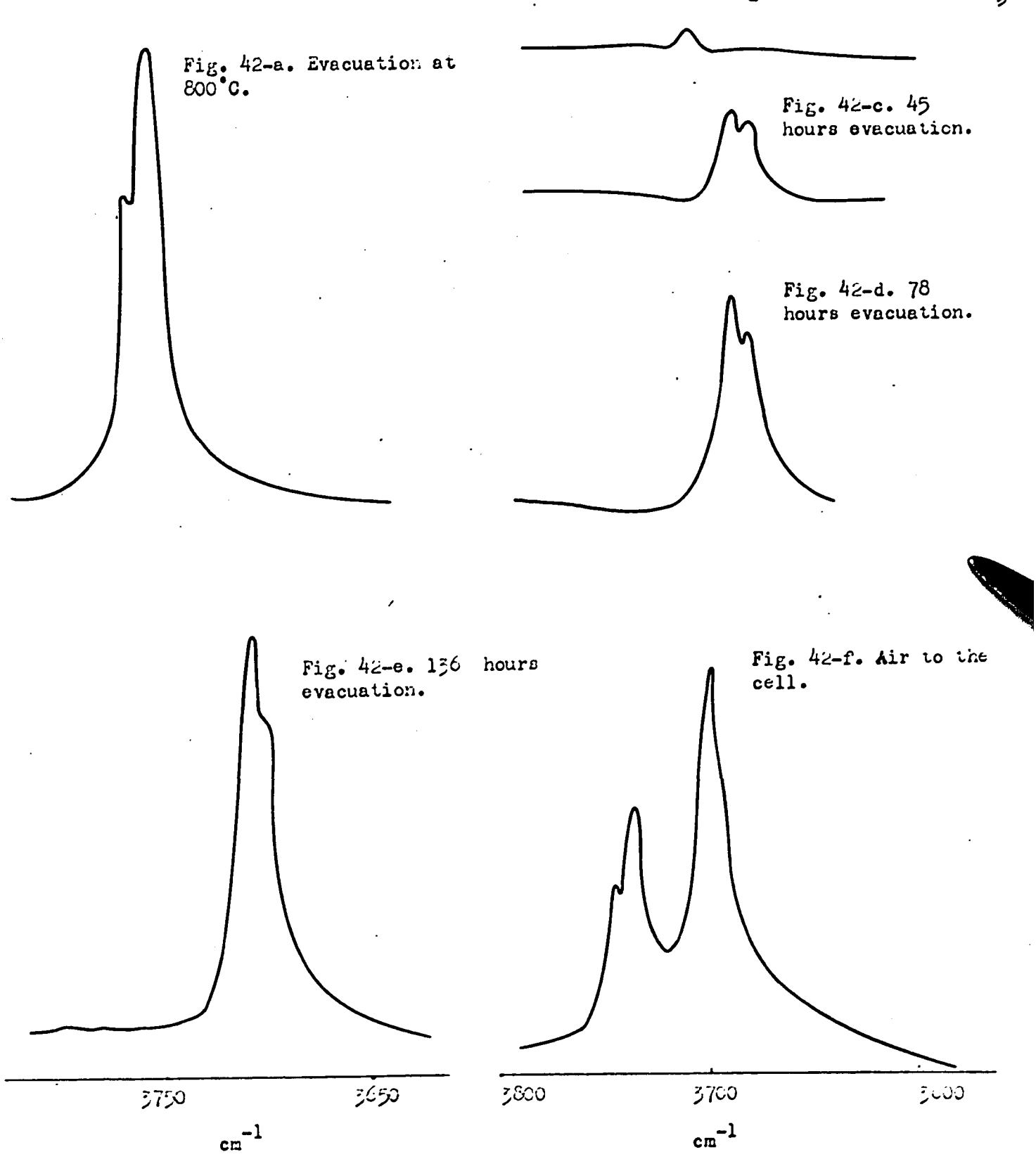


Figure 42. 1.0 mm. $B^{10}Cl_3$ adsorbed on silica. exchanged silica.

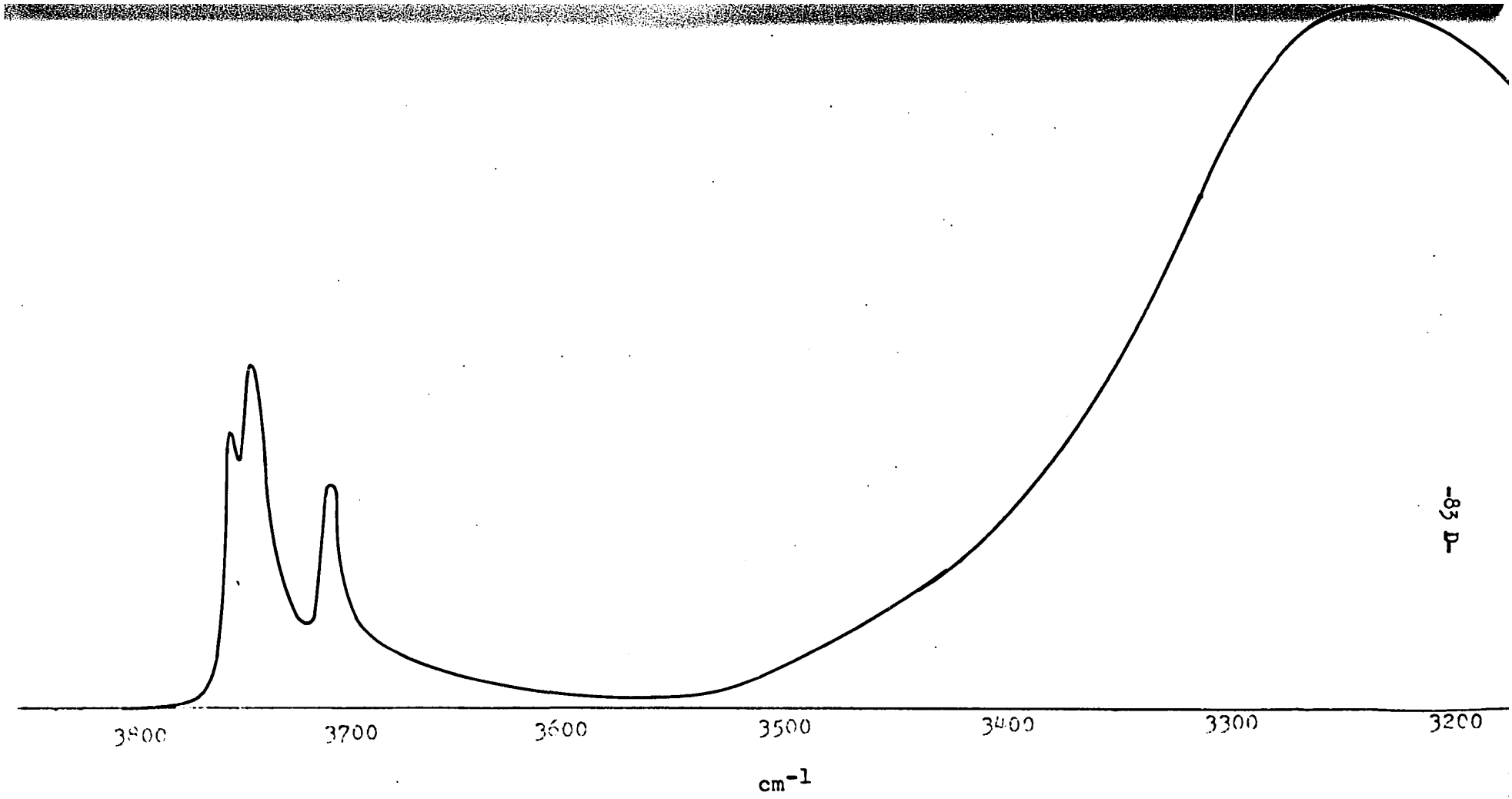


Fig. 42g Air to the cell for 24 hours

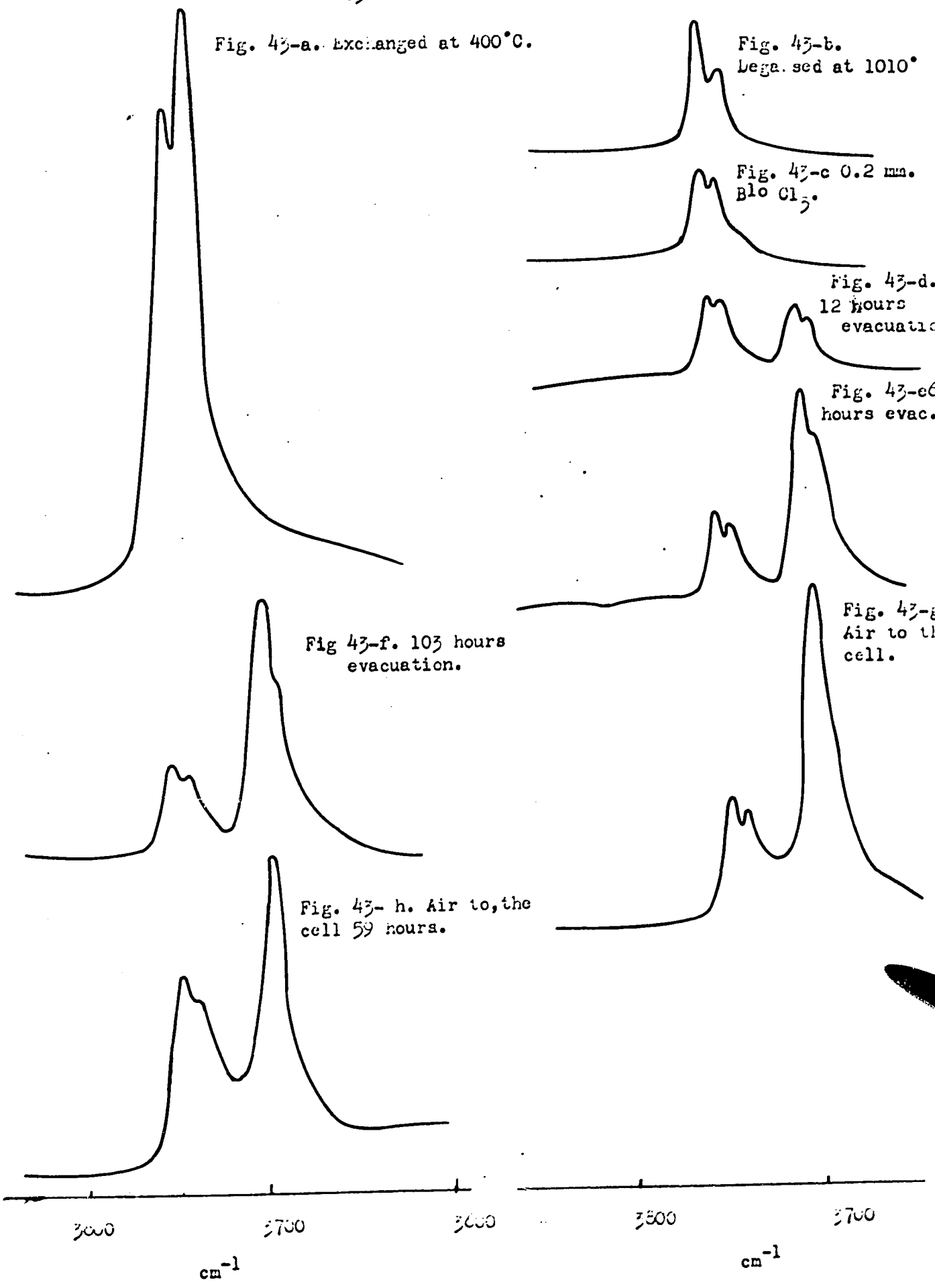
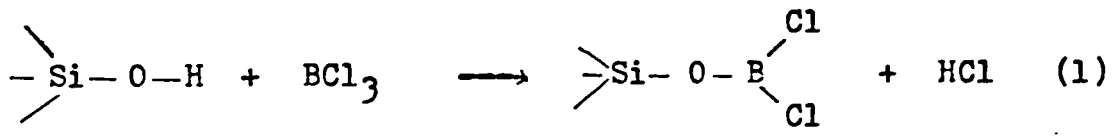


Figure. 43. 0.2 mm. $B^{10}Cl_3$ adsorbed on H_2O^{10} exchanged silica.

DISCUSSION

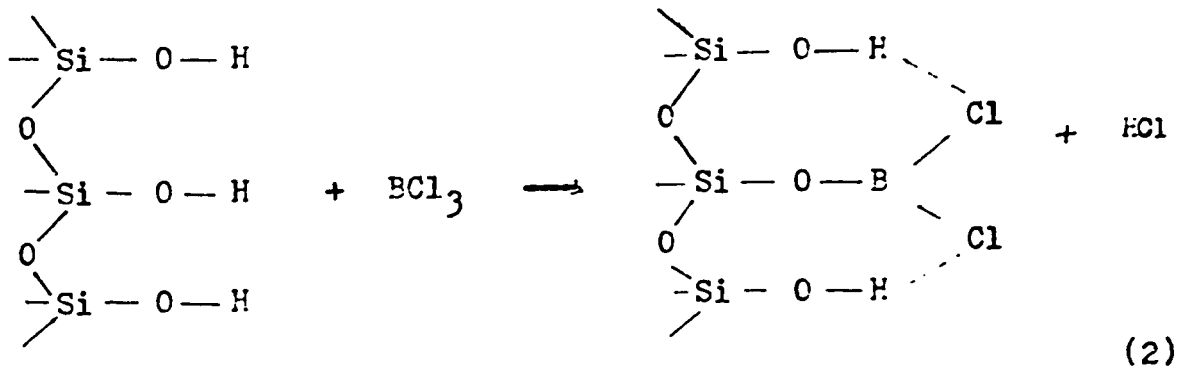
Boron Inchloride adsorbed on silica

The BCl_3 adsorption experiments were carried out originally to gain additional information concerning the nature of BCl_3 adsorption; however, the unique behaviour of BCl_3 on silica demands a mechanism quite different from that of BF_3 adsorption. The initial reactions of BCl_3 on silica will probably be analogous to the BF_3 reactions. Firstly the single isolated surface hydroxyl groups react with one molecule of BCl_3 to produce $Si\text{-}O\text{-}BCl_2$ and gaseous HCl.



(A)

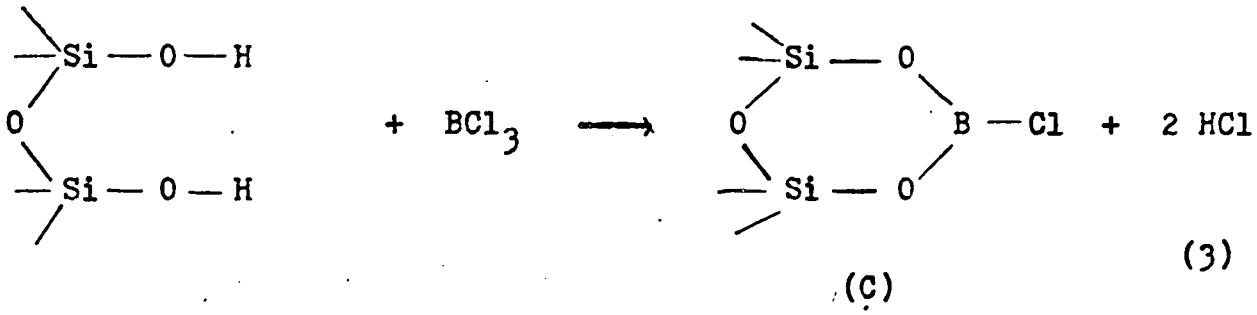
On low temperature heated silica samples, where adjacent or geminal hydroxyls are probably present, two types of reactions may take place to produce three adsorbed species. One BCl_3 molecule may react with one hydroxyl via reaction (1) and the remaining two chlorine atoms on the boron atom may hydrogen bond weakly with the H atoms on the adjacent hydroxyl groups:



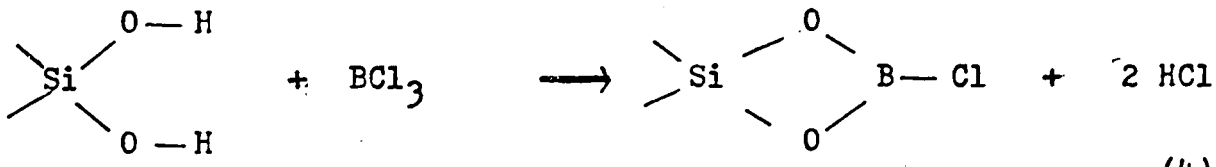
(B)

(2)

Secondly two chlorine atoms may react to form species C and D and two molecules of HCl.

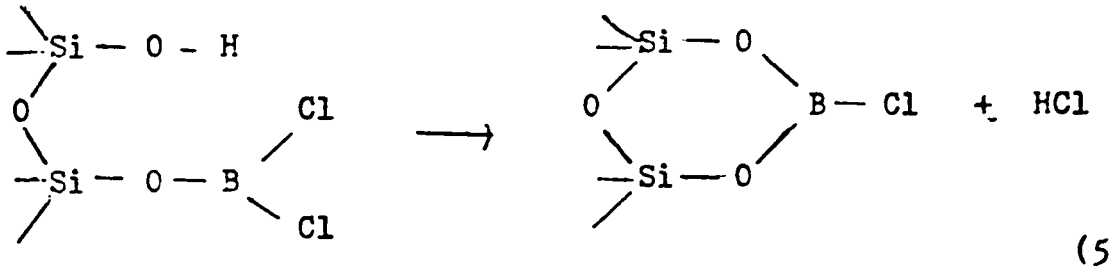


(C) (3)



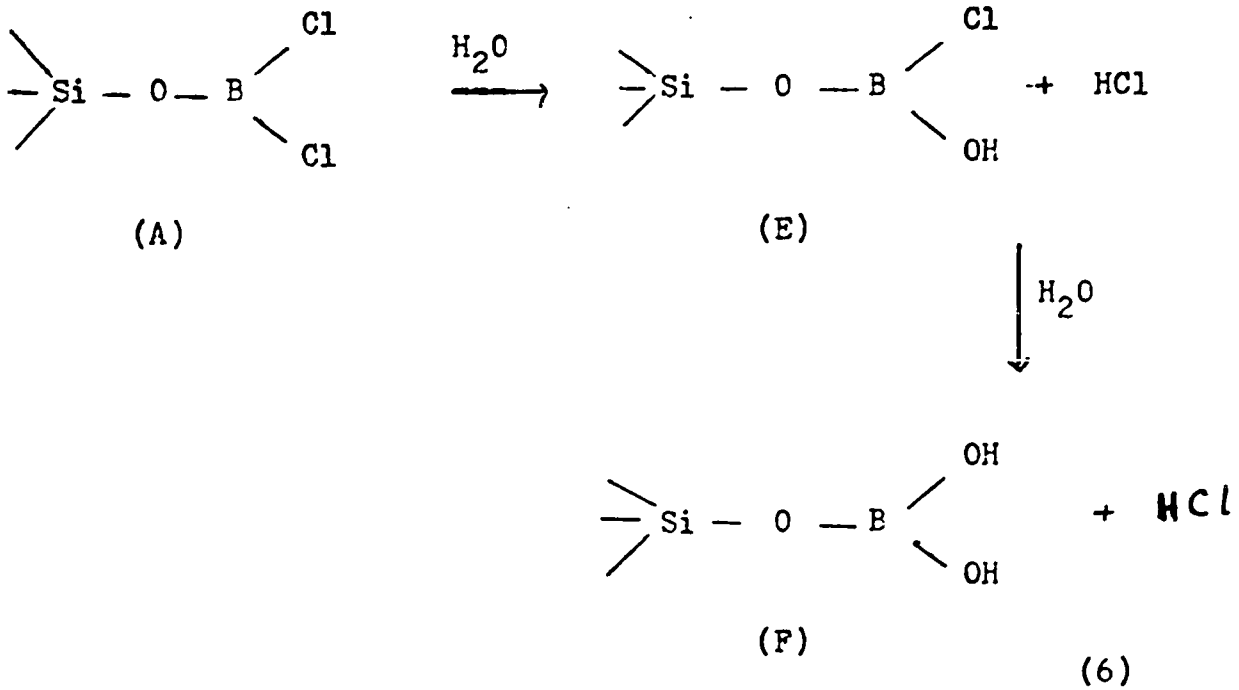
(D) (4)

Also, the species A can be converted to species C on reacting with an adjacent Si-O-H:

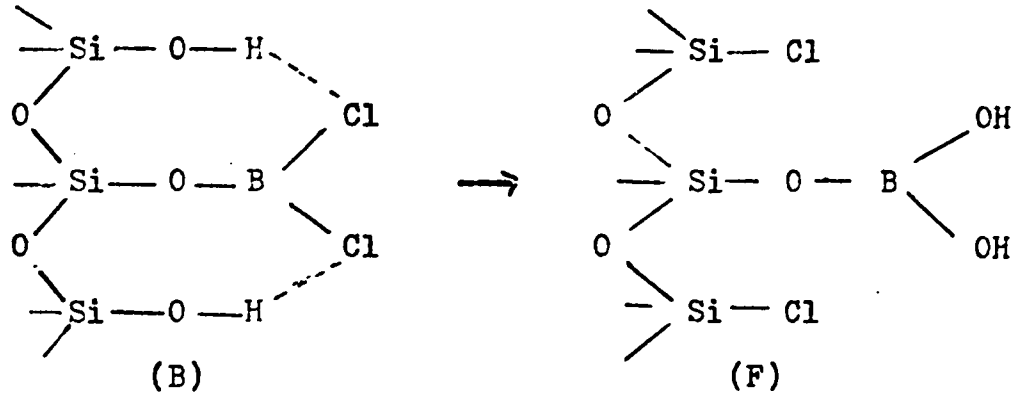


(A) (C) (5)

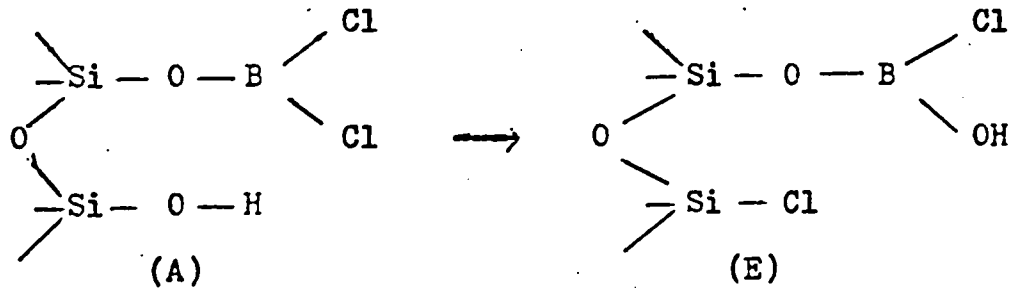
The reactions 1-5 are analogous to those occurring with BF_3 adsorption and can explain the disappearance of the initial 3749 cm^{-1} silanol band. However they still do not account for the absence of the Si-O-H band and the growth of the 3700 cm^{-1} B-O-H band on evacuation. It is known that BCl_3 reacts more readily with water forming boric acid $B(OH)_3$, whereas the complete hydrolysis of BF_3 occurs less readily since BF_3 can form mono and dihydro adducts $BF_3 \cdot H_2O$ and $BF_3 \cdot 2H_2O$ (53). Consequently, the chlorine atoms of a BCl species attached to the surface will be more reactive to H_2O and OH than the fluorine atoms present in a BF species. Therefore, a larger number of reaction products are probably possible with adsorbed BCl_3. The following are the reactions that may take place between the chlorine atoms and the surface O-H groups or 'H_2O'.



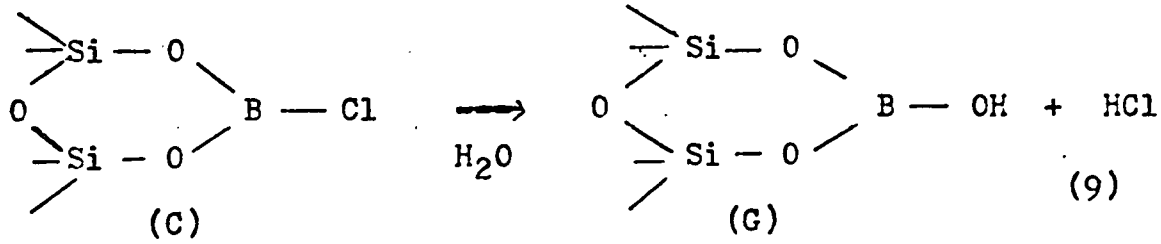
(6)



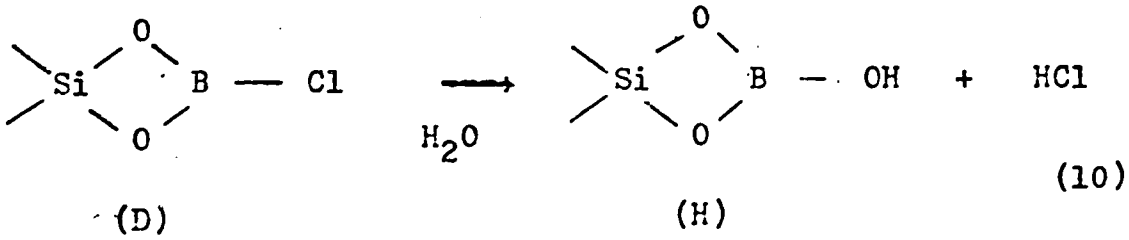
(7)



(8)



(9)



(10)

The growth of the B-OH band and the gradual disappearance of the initial Set A bands indicate that any or all of the reactions (6-10) may take place. The formation of the Si-Cl group via reactions 7 and 8 is not so remarkable since the surface OH group may exchange with a chlorine atom to form

Si-Cl. It has been postulated that on reacting Cl-Si $(CH_3)_3$ with Si-OH, a replacement reaction takes place (37)

$$Cl\text{-}Si\text{-}(Me)_3 + \geq Si\text{-}O\text{-}H \rightarrow \geq Si\text{-}Cl + OH\text{-}Si\text{-}(Me)_3$$

The Si-Cl band is found in the 625-415 cm^{-1} region; (63) no bands could be observed in this region with the apparatus used. However the surface Si-Cl band, if present, may have shifted to a higher frequency and have become undetectable against the silica background bands. What is not easily explained is that in the presence of 'H_2O' the chlorine atom in Si-Cl should again react to regenerate Si-O-H; instead, only a minute increase in the 3749 cm^{-1} silanol band is observed on evacuation (Fig. 28). This may be due to several reasons. Firstly, only a small number of these Si-Cl groups are possibly produced which may rehydrolyze to give the small increase in the Si-OH band. Secondly, with a small amount of 'H_2O' available, the hydroxylation of the B-Cl groups are preferential to that of the chlorine atom in Si-Cl. Lastly the hydrolysis of Si-Cl may be very difficult with small amounts of 'H_2O' or due to steric factors in presence of a neighboring large BCl_2 and $B(OH)_2$ groups.

In the previous attempts to study BCl_3 on silica, no reports of the 1600-1250 cm^{-1} region have been given. From studies of boron, oxygen and chlorine compounds it is known that B-O stretching modes absorb in this region (Tables 4 and 8). The seven possible species (A, C-H) produced on adsorbing

BCl_3 and on subsequent evacuation can give rise to several B-O and B-Cl stretching modes (Table 9). Because of the complexity of the spectra and the absence of many model compounds for purposes of comparison, the band assignments to be made are tentative and are derived from the spectra of similar compounds containing boron, oxygen and chlorine atoms.

In comparing tables 4 and 8, it is seen that the B-O asymmetric stretching modes of non-cyclic compounds are at a lower frequency than the corresponding bands of cyclic boron-oxygen containing compounds. The initial set of bands (Set IV), produced on adsorbing BCl_3 to silica, lie at a frequency lower than 1400 cm^{-1} and might be attributed to the B-O stretching mode of species A ($Si-O-BCl_2$). Further, the splitting of the Set IV bands to two bands at lower frequencies, in the spectra of H_2O^{18} exchanged silica samples, indicates that the 1385 and 1365 cm^{-1} (Set IV) bands are produced by oxygen containing species. Table 5 shows that the B-O stretching frequencies of cyclic compounds occur in the range of 1490-1400 cm^{-1} and since most of the set V bands are in this same frequency region, it is possible that some of these bands, observed on evacuation, may be due to the B-O stretching modes of cyclic surface species e.g. species C, G and H. The set V bands may also contain the B-O bonds due to non-cyclic species e.g. $Si-O-B\begin{smallmatrix}OH\\Cl\end{smallmatrix}$ and $Si-O-B(OH)_2$. It is

TABLE 8

B-O symmetrical and asymmetrical stretching frequencies of some boron oxygen containing compounds [79]

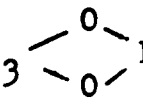
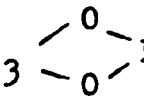
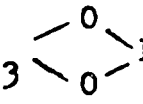
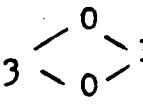
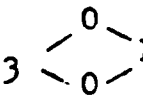
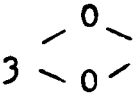
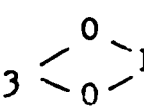
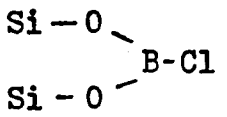
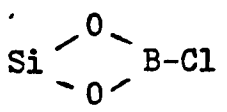
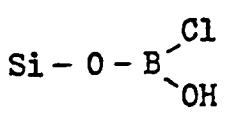
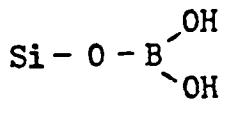
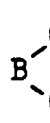
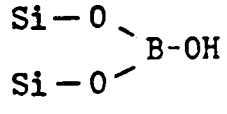
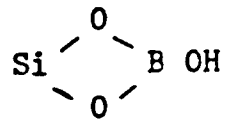
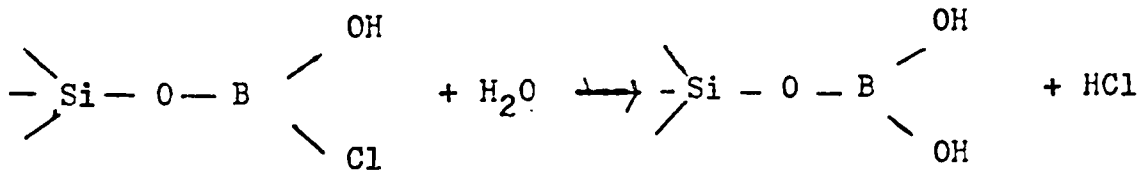
Compound	B(O)O sym str. cm^{-1}	B(O)O asym. str. cm^{-1}
$(CH_2)_3$  B Cl	1220	1490
$(CH_2)_3$  B-O C_2H_5	1210	1487
$(CH_2)_3$  B-O C_6H_5	1222	1488
$(CH_2)_3$  B C_6H_5	1040	1450
$(CH_2)_3$  B NCS	1215	1487
$(CH_2)_3$  B NH C_2H_5	1121	1466
$(CH_2)_3$  B-O(CH_2)Cl	1222	1486

TABLE 9

The stretching vibrational modes of the possible species produces on BCl_3 adsorption

	Species	B-O str.	B Cl str
(A)	$Si-O-BCl_2$	B-O str.	BCl_2 sym. str. asym. str.
(C)		B-O sym. str. asym. str.	B-Cl str.
(D)		B-O sym. str. asym. str.	B-Cl str.
(E)		B-O str. in Si-OB str. in B-O-H	B-Cl str.
(F)		B-O str.  sym. str. asym. str.	
(G)		B-O str.  sym. str. asym. str.	
(H)		B-O str.  sym. str. asym. str.	

not unexpected that the species containing hydroxyl groups attached to the boron atom will exhibit B-O stretching bands at frequencies higher than the corresponding bands produced by the species A ($Si-O-BCl_2$), where only chlorine atoms are adjacent to the boron band, since the chlorine atom is heavier than the 'OH' group. Assuming that the set IV bands belong to species A and the set V bands to species C-H, it can be concluded that the removal of the set IV bands and the growth of the set V bands probably corresponds to the replacement of chlorine groups by 'OH' groups and the conversion of the non-cyclic species to cyclic species is a reactions 6-10. The growth of the 1455 and 1410 cm^{-1} bands in set V together with the growth of the 3700 cm^{-1} B-O-H band can be attributed to the further hydrolysis of intermediary surface species on prolonged evacuation e.g.



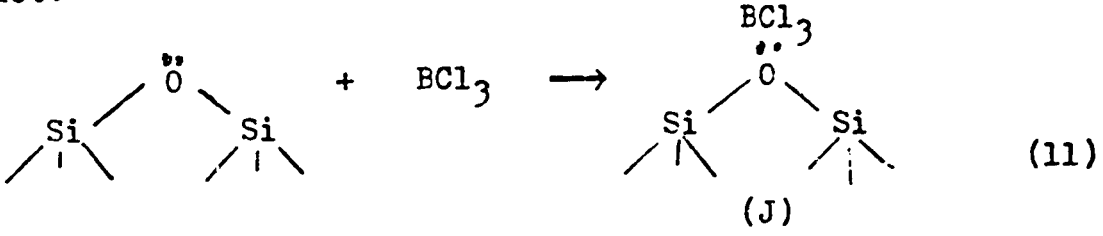
(F) (E)

A greater number of bands are to be expected if all the species in Table 7 were present. However, some of the bands, if present, may be overlapping and the weak bands may be masked by the stronger ones.

The BCl_2 asymmetric stretching frequencies are found in

the 900-1000 cm^{-1} region (Table 10); the 950 cm^{-1} band (Table 7) that is produced together with the Set IV bands on adsorbing B^nCl_3 to silica samples heated at temperatures both above and below 1000°C can be assigned to the B^nCl_2 asymmetric stretching frequency of species A. The corresponding band due to $B^{10}Cl_2$ is at a higher frequency and is masked by the silica background absorption bands. Although the B-Cl stretching modes in $ClB(OCH_3)_2$, $ClB(CH_3)_2$ and BF_2Cl have been reported to occur in the 570-700 cm^{-1} region (Table 7), Devlin and Latimer [56] have assigned the B-Cl stretching mode of trichloroboroxine $(BOCl)_3$, a cyclic compound, to a band at 1037 cm^{-1}. Further, Bellamy [64] et al reports that the spectrum of alkylphenyl chlorobornites, e.g. $CH_3\text{-}O\text{-}B\langle^{Cl}_{C_6H_5}$, exhibits a band at 900 cm^{-1} attributable to the B-Cl stretching mode. The 928 and 933 cm^{-1} bands produced on adsorbing B^nCl_3 and $B^{10}Cl_3$ respectively on silica samples evacuated at temperatures below 1000°C can possibly be assigned to the B-Cl stretching mode of species C. The absence of these bands in the corresponding spectra of silica samples evacuated above 1000°C is possibly due to the fact that high temperature heated surfaces may not contain any adjacent hydroxyls, required to produce species C.

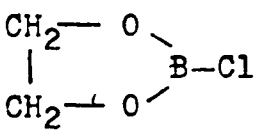
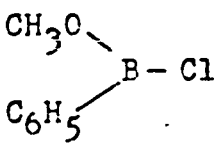
The Si-O-Si bridges, possibly present on high temperature heated silica surfaces, may react with BCl_3 to give a surface adduct:



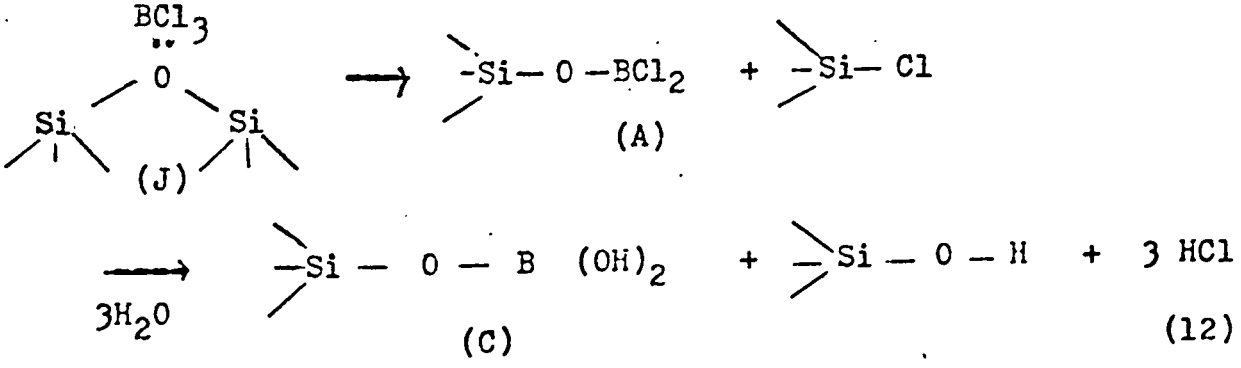
(J) (11)

TABLE 10

B-Cl Stretching Frequencies of Some boron and oxygen containing compounds

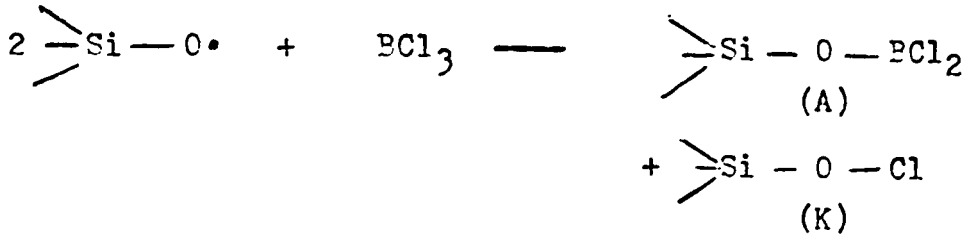
Compound	B-Cl sym str. cm^{-1}	B-Cl asym str. cm^{-1}	Ref.
$B^{10}Cl_3$	471	994	49
$B^{11}Cl_3$	471	954	49
$B^{10}FCl_2$	557	1031	52
$B^{11}FCl_2$	554	993	52
$Cl_2B(OCH_3)$	546	960	75
$ClB(OCH_3)$	630		75
$B^{10}F_2Cl$	696		52
$B^{11}F_2Cl$	701		52
$Cl_3B_3O_3$	1037		56
Si O BCl_2	701	900	80
B_2Cl_4		917	81
$(C_6H_5)_2BCl$	895		82
$(CH_3)_2$ BCl	579		83
	925		84
	900		64

The $C_6H_5N{:}\ BCl_3$ and $C_5H_{10}NH{:}\ BCl_3$ [65] addition compounds have been reported to exhibit B:N bands in the 1250-1100 cm^{-1} region. A band at 1190 cm^{-1} in the spectrum of $Cl_3PO{:}\ BCl_3$ has been assigned to the stretching mode of the B:O bond [23]; the corresponding B-Cl bands have been assigned in the 600-700 cm^{-1} region. No other infrared spectroscopic data are available to date on the frequencies of the B:O coordinate bond. The 922 and 913 cm^{-1} bands (Table 7), that are produced on adsorbing $B^{10}Cl_3$ and $B^{n}Cl_3$ respectively to silica samples evacuated at temperatures above 1000°C might be assigned to the B:O stretching mode in species J. However, this assignment is very speculative and can be verified by comparing the B:O band in BCl_3 adducts. The observed gradual disappearance of these five bands at 952, 933, 928, 922 and 913 cm^{-1} may represent the removal of the species A, C and J via various reactions e.g.



(12)

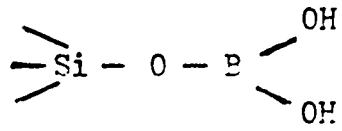
The Si-O type free radicals, if present on the high temperature heated silica surface may also react with BCl_3 via the following reaction:



(13)

The O-Cl stretching frequency in HOCl has been assigned at 739 cm^{-1} (66) and in Cl_2O at 630 cm^{-1} (67) and 945 cm^{-1} (68).

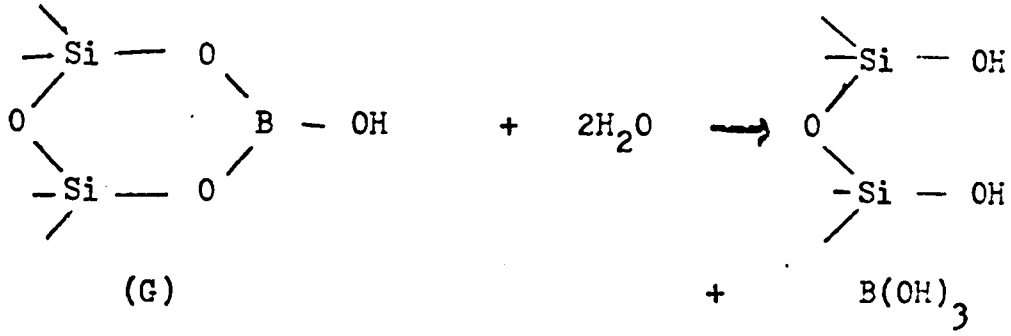
The borate ion in $LaBO_3$ and $ScBO_3$ exhibits a band at 939 cm^{-1} which has no isotopic shift with B^{10} or B^{11} substituted compounds (69). The 940 cm^{-1} band produced on prolonged evacuation (Table 7) of the BCl_3 treated silica sample also exhibits no isotope effect. This band may be attributed to the skeletal vibrations of a BO_3 group in species F.



(F)

On prolonged contact with air, the hydrolysis of species (F) to H_3BO_3 may result in the observed disappearance of the 940 cm^{-1} band. The set VI bands, which are at the same frequencies as the set III bands (Tables 1 and 6) indicate that same types of surface species are produced on adding air to either BF_3 or BCl_3 treated silica samples. The 1475 and 1420 cm^{-1} bands in set VI and the 880 cm^{-1} bands produced on adding

air again suggest that one of the hydrolyzed products may be boric acid formed via various reactions, e.g.



(G) + $B(OH)_3$

The hydrolysis of the various surface species may result in the initial increase in the 3700 cm^{-1} B-O-H band on adding air; the subsequent lowering of the 3700 cm^{-1} band intensity on greater contact with air is probably due to the hydrogen bonding of the B-O-H groups with water or neighboring hydroxyls. The 3690 cm^{-1} band, that grows with the 3700 cm^{-1} B-O-H band on evacuating a H_2O^{18} exchanged silica sample to which BCl_3 has been added (Fig. 42), can be assigned to the O-H stretching modes of B-O^{18}-H groups. The removal of the 3690 cm^{-1} band on prolonged contact with air, indicates that the O^{18}-H group in the surface B-O^{18}-H species can be exchanged with H_2O^{16} at room temperature. Whereas, the stability of the accompanying 3738 cm^{-1} Si-O^{18}-H band confirms the earlier observation that the surface silanols do not exchange with H_2O^{18} at room temperature.

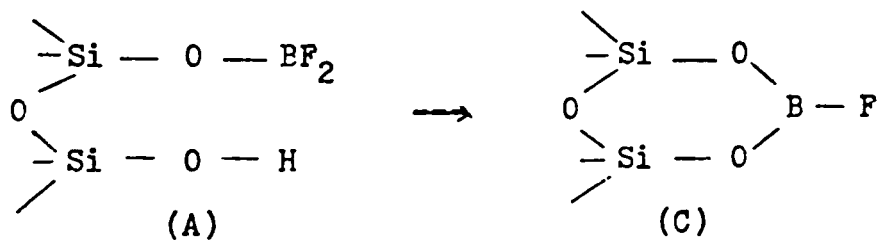
The maximum intensity of the B-O-H band on evacuation was always found to be greater in the spectra of low temperature

heated surfaces than in the spectra of high temperature heated surfaces (Fig. 39). Fewer active sites are possibly present on high temperature heated surfaces for the following reasons. Firstly, the weak 3749 cm^{-1} Si-O-H band indicates that a small number of silanols are present. Secondly, the surface area is known to decrease when silica is heated at temperatures greater than 1000°C. Consequently, a smaller number of BCl_3 molecules will be adsorbed which will then result in a smaller number of BOH groups. A supporting evidence is the observation that the spectra of high temperature heated surfaces exhibited less intense, well resolved set V bands. Whereas, the corresponding spectra of low temperature heated surfaces show more intense unresolved bands. The observed frequencies and their corresponding vibrational modes of the possible surface species formed on adsorbing BCl_3 on silica are listed in Table 11.

The growth of the 3749 cm^{-1} Si-O-H fundamental band on evacuating silica samples that have been previously evacuated at 1020°C to almost completely remove this band suggests that a certain amount of 'H_2O' is regenerated when silica samples are evacuated at room temperature. This is not due to a leak in the cell because if a silica sample is exposed to D_2O vapour in order to completely replace the 3749 cm^{-1} band by the Si-O-D band at 2760 cm^{-1} and is subsequently evacuated at 1020°C to

remove this later band, then on further evacuation at room temperature, only the growth in the Si-O-D band is observed. Moreover, the source of this 'H_2O' is probably from the walls of the reaction cell as opposed to the bulk of the silica sample. For, if a new silica sample is introduced, after the above experiment, then even after prolonged heating and evacuation, as previously described, a slow growth of the Si-O-D band still occurs.

It should be pointed out that when BF_3 or BCl_3 is adsorbed on a silica sample which has been evacuated at temperatures greater than 1000°C, then the 'H_2O' causes spectral changes only in the case of adsorbed BCl_3. Two factors contribute to this: firstly, the high temperature heated surface becomes somewhat annealed so that the number of sites that can refurnish the Si-O-H groups are reduced with high temperatures of dehydration. Since the reactions following BF_3 adsorption involve hydrolysis of the initial species A with surface silanols, a decrease in the sites that can produce the Si-O-H groups results in a smaller number of species A from being converted to species C.



(A) (C)

Secondly, the initial species formed on BCl_3 adsorption can react directly with the available water and undergo change.

Therefore, on high temperature heated surfaces containing small numbers of surface silanols, the initial species $Si-O-BCl_2$ can still be removed to give various hydrolyzed products.

TABLE 11

Observed frequencies of BCl_3 adsorbed on silica

Frequency cm^{-1}	Assignment	Species
3700	O^{16}-H str.	B-O^{16}-H
3690	O^{18}-H str.	B-O^{18}-H
1395	O^{16}-B^{10} str.	O^{16}-$B^{10}Cl_2$
1365	O^{16}-B^{11} str.	O^{16}-$B^{11}Cl_2$
1367	O^{18}-B^{10} str.	O^{18}-$B^{10}Cl_2$
1333	O^{18}-B^{11} str.	O^{18}-$B^{11}Cl_2$
952	B^{11} < Cl asym. / Cl str.	O-$B^{11}Cl_2$
933	B^{10}-Cl str.	$O_2B^{10}Cl$
922	B^{11}-Cl str.	$O_2B^{11}Cl$

Boron halides adsorbed on various oxide surfaces

It can be seen from Tables 5 and 6 that the infrared bands due to the symmetrical stretching modes of BO_2 groups occur in the 1250-1100 cm^{-1} region. The surface species formed on adsorbing BF_3 and BCl_3 on silica may also exhibit similar BO_2 bands which cannot be observed against the totally absorbing silica background spectrum on this region (Fig. 6). Therefore, spectroscopic investigations were carried out with various other oxides, that are known to be transparent to infrared radiation in the 1650-1110 cm^{-1} region, in an attempt to study the symmetrical stretching vibrational bands.

Alumina (Al_2O_3, Alon-C) could not be pressed into pellets in the manner used for silica as it tended to stick to the surface of the steel die. 50 mg. of alumina were placed between two paper discs and were pressed into pellets; the paper was then burnt off in a furnace at 500°C in the presence of O_2. Pellets so formed exhibited no observable contamination of the surface. Alumina has a strong band from 3695 to 3100 cm^{-1} region and is very transparent to infrared radiation upto 1250 cm^{-1}; from 1250 cm^{-1} to 1000 cm^{-1} the transparency decreases and the surface becomes totally opaque beyond 1000 cm^{-1}. The band at 3695-3100 cm^{-1} can be removed on evacuating the pellet at 500°C. On adsorbing BF_3 a broad band from 1450-1270 cm^{-1} and with BCl_3 a band from 1440-1230 cm^{-1} were observed. In some BF_3 adsorption experiments the broad band was resolved into strong peaks at 1440, 1422 and 1379 cm^{-1}.

On evacuation, both the 1500 cm^{-1} region and the 3695-3100 cm^{-1} region bands grew in intensity. No conclusions can be drawn from these spectra since the diffuse band in the higher frequency region suggests that various other types of active sites, apart from the hydroxyl groups, are probably present on the surface that may produce, on adsorption types of species different from those formed on the silica surface.

Magnesium Oxide (MgO), produced by burning magnesium ribbon in air, were collected on the sides of a NaCl disc (2.5 cm diameter). The disc was then placed in a infrared cell described by Morrow. (70) Magnesium oxide was observed to be about 70% transparent to infrared radiation from 1650-800 cm^{-1}. However, strong carbonate bands were present at 1430, 1380 and 1060 cm^{-1} that could not be removed on evacuating at room temperature, at various other temperatures, or by heating the pellet in presence of O_2. On adding either BF_3 or BCl_3, no new bands were observed in the spectrum.

Zinc oxide (ZnO) powder could not be pressed into pellets as it also tended to stick to the surface of the die. The oxide was mixed in ether and sprayed on to the surface of the NaCl disc. The disc was then placed in the same cell used for MgO experiments and its spectra were recorded. ZnO was found to be very transparent to infrared upto about 1000 cm^{-1} and exhibited strong carbonate bands at 1370 and 1340 cm^{-1}.

On evacuating at 420°C, these bands were removed and the surface was about 60% transparent. On adsorbing BF_3 or BCl_3 to such a surface, no bands were observed. Because both MgO and ZnO have large particle sizes, a heavy coating of the NaCl surface, produced excessive scattering of the incident radiation that resulted in a totally opaque background spectrum. The amount of material used had to be adjusted to obtain a transparent background. The absence of any bands on adsorbing boron halides on either ZnO or MgO surfaces may have been due to the fact that on the comparatively small amounts of oxides coated on the disc, to obtain a suitably transparent background, only a limited amount of boron halides could be absorbed which were not sufficient to produce observable bands due to the surface species.

The rutile form of titanium dioxide (TiO_2) was pressed into self-supporting discs and its spectra were recorded. Titania was about 60% transparent in the 1650-1000 cm^{-1} region and exhibited strong carbonate bands at 1600, 1440 and 1400 cm^{-1}. On evacuating the sample at various temperatures in presence of O_2, the sample assumed a purple colour and its transmission was reduced to almost zero. It is seen that from these experiments no information could be obtained on the bands produced on boron halide adsorption.

CONCLUSION

The data presented indicate that both BF_3 and BCl_3 are chemically adsorbed on silica at room temperatures and that the surface is possibly heterogeneous with respect to boron halide adsorption. On low temperature heated surfaces, silanols are probably the main active sites. Whereas on high temperature heated surfaces, the silanols may be totally removed and only the Si-O and the Si-O-Si types of sites may be present; however, a combination of any of these sites is also possible. BX_3 may react with the Si-O· site to produce X_2:

$$2 \geq SiO\cdot + 2\,BX_3 \longrightarrow 2\,SiO\text{-}BX_2 + X_2$$

An identification of X_2 in the product gases, may indicate the presence of SiO groups. Most other reactions will probably give similar surface species with either Si-O or Si-O-H and the identification of the product gases may also be difficult. The reactions with alcohols may take place via the following mechanisms:

$$\geq Si\text{-}OH + ROH \longrightarrow \geq Si\text{-}O\text{-}R + H_2O$$

$$\geq SiO\cdot + ROH \longrightarrow \geq Si\text{-}O\text{-}R + OH$$

The reaction of diazomethene with silica, to produce surface methoxy groups, requires the H atom on SiOH

$$\geq Si\text{-}OH + CH_2N_2 \longrightarrow \geq SiOCH_3 + N_2$$

In the absence of SiOH such a reaction may not take place. Consequently, infrared spectroscopic investigation of silica treated with CH_2N_2 may provide significant information concerning the presence or absence of silanols on high temperature heated surfaces.

A spectroscopic study of boron trichloride adducts e.g. $(C_2H_5)_2\ O{:}BCl_3$ may provide information concerning the formation of boron halide addition compounds with Si-O-Si bridges. Also determination of the heats of adsorption of BCl_3 or BF_3 adsorbed on silica samples previously evacuated at various temperatures may indicate the degree of surface heterogenity with respect to various types of active sites. Further, a study of the infrared spectra of model compounds such as H_3 Si-O-BCl_2 and H_3 Si-O-$B(OH)_2$ are necessary in order to assign the bands produced on BCl_3 adsorption to their respective species.

Various inorganic chlorides have been used to study the distribution of different kinds of hydroxyl groups on silica. Armistead et al [48] attempted to determine the number of paired hydroxyls on the surface by adsorbing $TiCl_4$, BCl_3 and $SiMe_2Cl_2$ on silica samples and measuring the amounts of chlorine remaining on the surface. It is possible to assume from the present work, that the hydrolysis of the chlorine atoms by the H_2O which desorbs from the cell walls may give a smaller number of surface chlorine atoms than that to be expected from

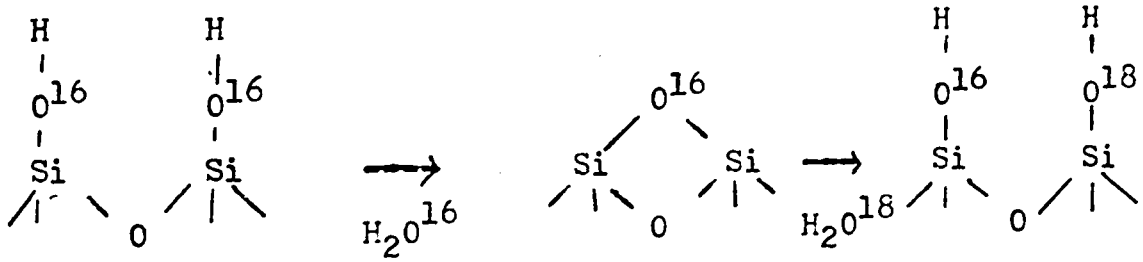
the existing number of single hydroxyls. This reactivity of chlorides towards water may make such calculations of paired and single hydroxyls untenable.

The maximum 70% exchange of the 3749 cm^{-1} silanol band suggests that either the hydroxyls present on the silica cannot be totally exchanged or that possibly two types of hydroxyls are present on the surface. There may be two possible mechanisms for H_2O^{18} exchange:

1) direct reaction with H_2O^{18}

(1)

2) formation of Si-O-Si bridges and rehydration with H_2O^{18}



(2)

On low temperature dehydrated silica samples where a large number of adjacent hydroxyls may be present, reaction (2) is possible, the formation of the $Si\text{-}O^{16}\text{-}H$ group may contribute to the residual 3749 cm^{-1} $Si\text{-}O^{18}\text{-}H$ band.

Reaction (1) may take place on surfaces dehydrated at

either high or low temperatures and complete exchange is to be expected if all the hydroxyls are equally exchangeable. However some hydroxyls may be inaccessible to the H_2O^{18} molecule due to steric hindrance. Secondly, the inability of the surface silanols to exchange at room temperature indicates that the removal of the surface OH groups may be necessary for exchange. This process will then be similar to the dehydration of isolated hydroxyls which probably takes place via mobile hydroxyl groups on the surface. The lowering of the 3749 cm^{-1} band intensity with increasing temperatures of dehydration and the presence of some silanols after high temperature dehydration (e.g. 940°C) suggests that the ease with which the hydroxyls can be removed may vary with different silanol groups. This difference may be due to the variation in the Si-O bond strength on the surface. As a result, the OH groups that can be more readily removed may also be exchanged more readily. Further, the fact that the exchanged silanols dehydrate at a faster rate than the residual $O^{16}H$ groups suggests that the later type of hydroxyls are thermally more stable than the exchanged ones. If at higher temperatures of dehydration, i.e. greater than 1000°C, all the OH groups can be detached from the surface, the reaction with H_2O^{18} at that temperature would result in total exchange. However, at higher temperatures, a large number of silanol bridges may form which may in the presence of H_2O^{18} form

Si-O^{16}-H groups via reaction 2. These Si-O^{16}-H groups may then produce a resultant Si-O^{16}-H band in the spectra of completely exchanged samples.

CLAIMS TO ORIGINAL RESEARCH

1. It has been shown that both BF_3 and BCl_3 are chemically adsorbed on the silica surface.

2. The spectroscopic behaviour, on evacuation, of the species formed by BF_3 adsorption has been shown to be different from that of the species obtained by BCl_3 adsorption. Mechanisms have been proposed to account for this difference in behaviour.

3. Some of the species, produced on BCl_3 and BF_3 adsorption, have been identified and the observed frequencies have been assigned to their vibrational stretching modes.

4. Spectroscopic evidence has been presented to show that the surface silanols exchange with H_2O^{18} and that the degree of exchange varies with experimental temperature.

5. It has been shown that the surface silanols cannot be completely exchanged with H_2O^{18} and that the exchanged silanols dehydrate more readily than the remaining silanols.

6. Mechanisms have been proposed that would account for the surface silanol exchange at various temperatures.

REFERENCES

1. B.M.W. Trapnell, Proc. Roy. Soc., A, 206, 39 (1951).

2. M. Hair, "Infrared Spectroscopy in Surface Chemistry", Marcel Dekker, New, York, 1967.

3. L.H. Little, "Infrared Spectra of Adsorbed Species", Academic Press, New York, 1966.

4. J.H. Taylor and C.H. Amberg, Can. J. Chem., 39, 535 (1961).

5. H.P. Leftin and M.C. Hobson, Advances in Catalysis, 14, (1963).

6. V.P. Kazansky and G.B. Pariisky, Kinetica i Kataliz, 2, 507 (1961).
C.A. 56, 6810f.

7. D.E. O'Reilly, Advances in Catalysis, 12, (1960).

8. A.V. Kiselev, Kolloid Zh., 2, 17 (1936).
C.A., 30, 6263^{9}.

9. P.C. Carman, Trans. Faraday Soc., 36, 964 (1940).

10. I. Shapiro and H.G. Weiss, J. Phys. Shem., 57, 219 (1953).

11. R.K. Iler, "The Colloidal Chemistry of Silica and Silicates", Cornell University Press, Ithaca, New York, 1955.

12. N.G. Yaroslavsky and A.N. Terenin, Dokl. Akad. Nauk., 6, 885 (1949).
C.A. 43, 7343h.

13. R.S. McDonald, J. Phys. Chem., 62, 1168 (1958).

14. J.B. Peri, J. Phys. Chem., 70, 2937 (1966).

15. A.V. Kiselev, "Structure and Properties of Porous Materials", Colson papers, Vol. 10., Butterworth, London, 1958.

16. J. Fraissard and B. Imelik Bull. Soc. Chim. Fr., 1710 (1963).
C.A. 60, 3518C.
17. J.A. Hockey and B.A. Pethica, Trans. Faraday Soc., 57, 2246 (1961).
18. G.J. Young, J. Colloid Sci., 13, 67 (1950).
19. J.J. Fripiat, M.C. Gastuche and P. Brichard, J. Phys. Chem., 66, 805 (1962).
20. M. Folman and D.J.C. Yates, Proc. Roy. Soc., A, 246, 32 (1958).
21. A.N. Sidorov, Russ. J. Phys. Chem., 30, 995 (1956).
C.A. 51, 12656h.
22. L.D. Belyakova and A.V. Kiselev, Zh. Fiz. Khim., 33, 1534 (1959).
C.A. 54, 8213b (1960).
23. T.C. Waddington and F. Klanberg, J. Chem. Soc., 2339 (1960).
24. N.W. Cant and L.H. Little, Can. J. Chem., 43, 1252 (1965).
25. J.J. Fripiat and J. Uytterhoeven, J. Phys. Chem., 66, 800 (1961).
26. G.A. Galkin, Sp. Zhdanov, A.V. Kiselev and V.I. Lygin, Kolloidn. Zh., 25, 1, 123 (1963).
C.A. 59, 140e.
27. V.A. Davydov, A.V. Kiselev and L.T. Zhuravlev, Trans. Faraday Soc., 60, 2254 (1964).
28. T.H. Elmer, I.D. Chapman and M.E. Nordberg, J. Phys. Chem. 67, 2219 (1963).

29. M. Folman, Trans. Faraday Soc., 57, 2000 (1961).

30. M. Baverez, B. Hatier, M. Bastick and J. Bastick, Bull. Soc. Chim. France, 6, 1298 (1964).

C.A. 61, 9165f.

31. M.V. Mathieu and B. Imelik, J. Chem. Phys. 59, 1189 (1962).

32. J.J. Fripiat and M. van Tongelen, J. Catalysis, 5, 158 (1966).

33. H.A. Benesi and A.C. Jones, J. Phys. Chem., 63, 179 (1959).

34. F.H. Hambleton and J.A. Hockey, Trans. Faraday Soc., 62, 1694 (1966).

35. C.G. Armistead and J.A. Hockey, Trans. Faraday Soc., 63, 2549 (1967).

36. J.B. Peri and A.L. Hensley Jr., Jour. Phys. Chem., 72, 2926 (1968).

37. M.L. Hair and W. Hertl, Jour. Phys. Chem., 73,2372 (1961).

38. A.V. Topchiev and L.A. Alyavidna, Dokl. Akad. Nauk., 119, 957 (1958).

C.A. 52, 17085b.

39. G.L. Hervert and C.B. Linn,

C.A. 58, 4363g.

40. T.V. Antipina and E.N. Ardonina, Zhur. Fiz, Khim., 33, 192 (1959).

C.A. 53, 21102i.

41. P.D. May and J.J. Kelly,

C.A. 52, 711g.

42. I.E. Neimark, R.Yu. Sheinfain and A.I. Kazantseva,

C.A. 55, 8699c.

43. V.A. Chermov and T.V. Antipina,

C.A. 58, 1927d.

44. A.V. Topchiev and A.P. Ballod, Dokl. Akad. Nauk., 90, 1051 (1953).

C.A. 49, 8024h.

45. A.A. Babushkin, C.A. 51, 17454f.

46. B.A. Morrow, Ph.D. Thesis, Cambridge University (1965).

47. K.H. Rhee and M.R. Basilla, J. Catalysis, 10, 243 (1968).

48. C.G. Armistead, A.J. Tyler, F.H. Hambleton, S.A. Mitchell and J.A. Hockey, J. Phys. Chem., 73, 3947 (1969).

49. R.E. Scruby, L.R. Lacker and J.D. Park, J. Chem. Phys., 19, 386 (1951).

50. Handbook of Preparative Inorganic Chemistry, 1, 220, Ed. G. Brauer, Academic Press, New York, (1963).

51. W.G. Spitzer and J.R. Ligenza, J. Phys. Chem. Solid, 17, 196 (1961).

52. L.P. Lindeman and M.K. Wilson, J. Chem. Phys., 24 242 (1956).

53. A.G. Massey, Advances in Inorganic Chemistry and Radio Chemistry, Vol. 10, Academic Press, New York (1967).

54. J.E. de Moor and G.P. van der Kelen, Der. Bun. Physik. Chem., 67, No. 4, 429 (1963).

55. J. Goubeau and K.H. Rowhedder, Ann. Chem., 604, 168 (1957).

C.A. 51, 16281f.

56. B. Latimer and J.P. Devlin, Spec. Acta., 21, 1437 (1965).

57. C. Morterra and M.J.D. Low, J. Phys. Chem., 73, 327 (1969).

58. A. Arkell, J. Am. Chem. Soc., 87 (18), 4057 (1965).

59. E.A.V. Ebsworth and M. Onyszchuk, J. Chem. Soc., 1453 (1958).

60. F. Matossi and H. Bluschke, Z. Physik., 108, 295 (1938).

61. D.E. Bethell and N. Sheppard, Trans. Faraday Soc., 51, ((1954).

62. R.R. Servoss and H.M. Clark, J. Chem. Phys., 26, 1175 (1957).

63. A.L. Smith, J. Chem. Phys., 21, 1947 (1953).

64. L.J. Bellamy, W. Gerrard, M.F. Lappert and R.L. Williams, J. Chem. Soc., 2412 (1958).

65. N.N. Greenwood and K. Wade, J. Chem. Soc., 1130 (1960).

66. K. Hedberg and R.M. Badger, J. Chem. Phys., 19, 508 (1951).

67. M.M. Rochkind and G.C. Pimentel, J. Chem. Phys., 42, 1361 (1965).

68. K. Hedberg, J. Chem. Phys., 19, 509 (1951).

69. N.C. Steele and J.C. Decius, J. Chem. Phys., 25, 1184 (1956).

70. B.A. Morrow, J. Sci. Instr., 43, 487 (1966).

71. G.M. Begun, W.H. Fletcher and A.A. Palko, Spec. Acta., 18, 665 (1962).

72. G.M. Begun and A.A. Palko, J. Chem. Phys., 38, 2112 (1963).

73. M. Taillandier and E. Taillandier, Spec. Acta., 25A, 1807 (1969).

C.A. 72, 7541x.

74. W.J. Lehman, T.P. Onak and I. Shapiro, J. Chem. Phys., 30, 1215 (1959).

75. W.J. Lehman, T.P. Onak and I. Shapiro, J. Chem. Phys., 30, 1219 (1959).

76. H.R. Snyder, M.S. Konecky and W.J. Lennarz, J. Am. Chem. Soc., 80, 3611 (1958).

77. D. White, D.F. Mann, P.N. Walsh and A. Sommer, J. Chem. Phys., 32, 488 (1960).

78. D. White and P.N. Walsh, J. Chem. Phys., 28, 508 (1958).

79. A. Finch and E.J. Pearn, Spec. Acta., 19, 1621 (1963).

80. M. Onyszchuk, Can. J. Chem., 39, 808 (1961).

81. D.E. Mann and L. Fano, J. Chem. Phys., 26, 1665, (1957).

82. S.H. Dandegonker, W. Gerrard and M.F. Lappert, J. Chem. Soc., 2872 (1957).

83. H.J. Becker, C.A. 47, 7896h.

84. J.A. Blau, W. Gerrard, M.F. Lappert, B.A. Mountfield and H. Pyszora, J. Chem. Soc., 380 (1960).