CHEMISORPTION OF ETHANOL

ON LITHIUM FLUORIDE

by

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ABSTRACT

The adsorption of gaseous ethanol on lithium flouride surfaces was studied. The orientation and structure of the adsorbed species were investigated by applying infrared techniques.

A ten-centimeter gas cell was used. The cell was evacuated by employing a glass vacuum system which was attached to a mechanical pump and a diffusion pump. Pure liquid ethanol was injected into the system and vaporized. The gaseous ethanol was collected in the cell at various pressures, then the cell was transferred to a Beckman IR 4 infrared spectrophotometer to obtain the spectra.

Exposure of LiF crystals to ethanol vapor gave infrared bands, for the surface species which were due to the C-H stretching in the CH_3 and CH_2 groups. In all cases studied the bands assigned to the CH_3 and CH_2 stretching shifted to a longer wavelength after adsorption. These bands are interpreted as indicating that the adsorption of ethanol molecules to the surface involved two-point mechanism.

I. INTRODUCTION

A fundamental understanding of catalysis requires a thorough knowledge of the nature of catalyst surfaces. Insight into the reaction mechanisms involved in catalysis would lead to a better understanding of the nature of catalyst surfaces and consequently facilitate the selection of more efficient catalysts.

Correlations of different kinds between the geometry of a solid surface and catalytic activity have been proposed by many investigators. In 1921 Langmuir (23) pointed out that the surface reaction would be quite retarded if the catalyst atoms were a little too far apart, or if their electrons were not mobile enough to permit the rearrangement of the electrons involved in the surface reaction. Langmuir concluded that the geometrical arrangement of the atoms on the surface of the catalysts is a factor influencing the activity of catalysts. Adkins (1) studied the decomposition of ethyl acetate at alumina surfaces and found that the formation of acetone requires a wider spacing of atoms on the catalyst surface than for the formation of an olefin. Consequently, he suggested that the catalytic activity of alumina may be conditioned by the distances between the aluminum atoms. In 1926 Burk (13) postulated that the separation of the atoms A

1

and B of the molecule A-B can be accomplished by a surface only if both atoms become attached to the surface. If the adsorbing atoms are separated by a distance somewhat greater than the A-B bond length, their attraction for A and B causes the link in the reactant to be ruptured.

Many investigators have proposed the existence of a relation between dislocations and catalytic activity. Among the pioneers who observed the effect of dislocation in catalytic activity were Eckell (15) and Cratty and Granato (14). Since then, other investigators have noticed the connection between dislocations and catalytic activity, but most of the observations have been of a casual nature and almost all of these lacked quantitative measurements. Recently, however, Hall and Rase (21) conducted a quantitative study and confirmed the existence of a connection between dislocations and catalytic activity. This experimental work consisted essentially of treating LiF crystals in different ways to produce different dislocation densities, measuring the dislocation densities and then determining the rate of the reaction in the precision microreactor apparatus. Hall concluded that a definite relationship exists between dislocation density and catalytic activity of LiF in the dehydrogenation of ethanol. He further proposed that the geometry of the ethanol molecule and the position of the fluorine atoms at the edge dislocation in Lithium fluoride suggest a particular orientation

of the adsorbed ethanol molecule at the dislocation. The
dimensions of the triangle formed by the alpha hydrogen
atoms and the hydroxyl hydrogen atom on the ethanol molecule
compare favorably with the dimension of the triangle formed
by the three fluorine atoms at the edge dislocation.
Adsorption with these triangles and adjacent would also
favor the dehydrogenation reaction.

In recent years there has been much speculation on
the nature and orientation of adsorbed species on the cata-
lyst surfaces. Blyholder and Neff (12) studied the structure
of surface species formed as a result of the exposure of
nickel to ethanol, methanol, ether, and water. They found
that at room temperature the most stable surface structure
formed by the above compounds is chemisorbed CO. However,
the exact structure of chemisorbed CO was not determined.
Blyholder and Bowen (11) obtained the infrared spectra of
sulfur compounds adsorbed on silica supported nickel. They
postulated that the major portion of chemisorbed molecules
are dissociatively adsorbed. From this they concluded that
metal-carbon bonds could be responsible for the tightly
held chemisorbed species. In the case of CO adsorbed on
rhodium, Yang and co-workers (33) interpreted their data in
terms of three types of structure:

1. Two CO molecules bonded to one surface Rh atom.
2. A single "linear" CO bonded to one Rh atom.

3. A "bridged" CO between two adjacent Rh atoms
   which already have a single "linear" CO bonded
   to each.

Eischens and co-workers (16) studied adsorption of CO on
Ni and Pd. They interpreted their spectra in terms of
two types of structure:

1. A "linear" CO occupying a single surface site.
2. A "bridge" CO between two adjacent metal atoms
   in the surface.

In spite of the many investigations concerning the nature
and the orientation of the adsorbed species, it is
apparent that at the present time very little direct
evidence is available on the structure and bonding of
these molecules.

Precise infrared studies of adsorbed species on
surfaces of known and simple crystal structure could
definitely lead to a better understanding of the nature
of catalyst surfaces. Lithium fluoride, with its simple
face centered cubic crystal structure, is quite suitable
for such studies since its mechanical properties and the
dislocations in its crystal structure are well known.
The infrared spectrum of ethanol is well established.
This, along with Hall's (21) work is the basis for
conducting an infrared study of the adsorbed ethanol
molecules on lithium fluoride surfaces. It was the

objective of this research to apply infrared techniques to a LiF-EtOH system to gain new insight into the mechanisms and geometrical aspects of adsorption and catalysis.

II. THEORY

Surface geometry was introduced as an important factor in heterogeneous catalysis in 1906 by Rasching (25). Although many investigations of the geometrical aspect in catalysis have been conducted since then, no clear picture of this effect has been confirmed. In order for this geometrical effect, and ultimately the phenomena of catalysis, to be fully understood, the actual configuration of the atoms in the solid catalyst and the arrangement of the adsorbed species on it must be elucidated.

Surface geometry will be discussed first in a brief introduction to the concept of active sites on catalysts, followed by a short section on the position of the molecules on the catalyst surface. In addition, the theory of infrared spectroscopy and its application in adsorption studies, the techniques developed by Eischens and Pliskin (17), will be briefly presented.

The Concept of Active Sites

Evidence for the existence of active sites has been gathered through observations in different aspects of catalysis. Wood (32), for example, found that the rate of recombination of hydrogen atoms was slow in a clear

glass tube. However, when the inner surface of the tube was scratched rapid catalysis took place at the scratch. This observation wasinterpreted by Taylor (27) as direct evidence that the strain of the surface atoms, due to the scratch, had been responsible for the observed catalytic action. Taylor (27) also interpreted the decrease in heat of adsorption as the catalyst surface becomes more completely covered as evidence for the existence of non-uniformity of the surface.

Other experimental evidence from studies conducted on catalyst poisoning (2), rates of catalytic reactions (28), and adsorption-desorption phenomenon (29) has also offered support for the concept that the catalyst surface is atomically non-uniform. The evidence indicating the lack of uniformity of the catalyst surface led Taylor (27) to put forward the idea of active sites. Taylor assumed these active sites to be limited parts of the surface with high activity. He further assumed that the constituent atoms in these active sites were quite loosely attached to the bulk of the catalyst so that they were more chemically active.

Although not all of the experimental evidence which led Taylor to the concept of active sites is conclusive, these observations provide a theme upon which much experimental investigation has been done.

The Position of the Molecules on Catalyst Surfaces

Most of the work on the position of molecules on catalyst surfaces has been done with the reaction of hydrocarbons and other organic molecules of different sizes. The concept of two-point adsorption was first postulated by Burk (13). On the basis of this concept many important geometrical conclusions have been drawn. Twigg and Rideal (31), for example, studied the chemisorption of ethylene on nickel. The nickel crystal has a face-centered cubic structure with a lattice spacing of 3.50 Å and a short nickel-nickel distance of 2.47 Å. The C-C spacing in ethylene is 1.54 Å and the Ni-C spacing is the same as carbonyl (1.82 Å). The chemisorbed ethylene molecule will fit on the close Ni-Ni spacing with very little distortion of the Ni-C-C angle from 109 degrees and 28 minutes. They concluded that on a metal surface where the interatomic distance ranges between 2.4 Å to 2.8 Å two-point adsorption of hydrocarbons can easily take place.

Herrington and Rideal (22), in explaining some of the main features of the ring-closing mechanism, postulated that the dimensions of the C-C spacing in aliphatic hydrocarbons, of the Mo-C bond, and the spacing of the Mo-Mo in the MoO_2 lattice strongly suggest that two-point adsorption

of two adjacent carbon atoms can take place without much distortion.

Beeck, Smith, and Wheeler (9) investigated the hydrogenation of ethylene on nickel films. These films were deposited either in a vacuum or in the presence of nitrogen gas at 1 mm pressure. Electron diffraction confirmed that the film deposited in the presence of nitrogen was oriented so that the (110) plane was exposed. They report that the activity of the oriented film was ten times the activity of the film deposited in a vacuum.

Beeck (7) studied the rate of the hydrogenation of ethylene over evaported porous films of some transition metals, and determined the correlation between activity and size of a unit cell. Rhodium, which has the most suitable spacing for two-point adsorption of olefins, was found to have the highest activity. In the same investigation, Beeck measured the rate of hydrogenation of acetylene. Pallacium proved to be the most active catalyst for the above reaction. This is in agreement with Adkins' postulation (1) that a wider spacing is required for acetylene adsorption.

Anderson and Avery (3) studied the isomerization of aliphatic hydrocarbons over evaporated films of platinum and palladium. From arguments based on the influence of the geometry of hydrocarbons on the reaction (4, 5, 8), they concluded that the surface intermediate for

isomerization and hydrocracing was 1-3 diadsorbed for C_3 and C_4 hydrocarbons, and 1-2 diadsorbed for ethane.

The amount of literature available on the position of molecules on catalyst surfaces is much greater than what has been presented here. This brief survey is given to indicate the importance of geometry of a catalyst surface and the position of adsorbed molecules.

Infrared Spectroscopy

The region of the electromagnetic spectrum which covers the range from 0.75 microns to 200 microns is known as the infrared region. This region is divided into three parts. The shorter and longer wavelength regions are referred to as the near- and far-infrared regions, respectively. The region between 2.5 and 16 microns is called the "infrared" region. The near- and far-infrared regions have not been probed to a great extent and as yet can not be used qualitatively.

Infrared spectroscopy is a powerful tool for the study of chemical bonds. Many authors use the analogy between molecules and the spring-ball system to show the fundamental principles involved in infrared spectroscopy. The motion of atoms and chemical bonds resemble that of a system of spring and balls in constant motion. Their

motion is composed of two components, namely, stretching and bending. The nature of the bonds, such as C-H or C-N, is not the only factor influencing the frequencies of these vibrations. These frequencies are also affected by the entire molecule and its environment. A similar situation is encountered in the spring-ball system where the vibration of the spring is influenced by damping forces. However, there is a difference between a molecule and the spring-ball system. The vibrational levels of a molecule are quantized; therefore, the infrared beam can be absorbed by a bond only if it has a frequency corresponding to that which is required to raise the energy level of that bond. This causes the amplitude of the particular vibration to increase suddenly, not gradually. If a molecule is irradiated by an infrared beam with a continously changing wavelength only certain regions of this beam will be absorbed by the molecule. The energy of these absorbed wavelengths excite the stretching and bending of the bonds. In the region of absorption, the intensity of the transmitted beam will be decreased. A recording of the intensity of the transmitted beam versus wavelength is called infrared spectrum. This spectrum is often presented in terms of wavenumber, instead of wavelength, which is equivalent and is just the number of waves per centimeter.

The atoms of a molecule are constrained to oscillate about their equilibrium positions by the valence forces which exist between them. The motions of these atoms can be described by an equation which is dimensionally similar to that which holds for simple harmonic vibrations, namely

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \qquad (2\text{-}1)$$

The reduced mass, μ, is calculated from the following relation

$$\frac{1}{\mu} = \frac{1}{m_2} + \frac{1}{m_1} . \qquad (2\text{-}2)$$

The force constant, k, is related to the vibrations by the following relation

$$v = \frac{1}{2} kx^2 . \qquad (2\text{-}3)$$

After substitution of the proper universal constants and simplification, equation (2-1) can be reduced to

$$\nu = 1307 \sqrt{\frac{k}{\mu}} \qquad (2\text{-}4)$$

where μ is expressed in dimensionless atomic mass unit (AMU) and k is used as a pure number.

When the values for k and μ in equation (2-4) are known, the absorption frequency for a particular atom pair can be determined by this equation. Barnes, Liddel, and Williams (6) have determined the absorption frequencies of

a number of atom pairs in organic compounds using equation
(2-4). They found this relation to give satisfactory
results.

When the value of the absorption frequency of a
particular band has been determined experimentally, equa-
tion (2-4) can be used to calculate the force constant k.
Published data (6) indicate that in general the value of k
increases as the equilibrium distance between the atoms
becomes shorter.

In spite of the fact that the frequencies of the
bonds in a molecule are affected by the molecular environ-
ment, some bonds do possess unique characteristics. Double
bonds, for example, have a larger spring constant, k, than
single bonds and the terminal hydrogen atoms in X-H type
bonds are especially light. Also, the frequencies of these
bonds are affected by the environment of the molecule to a
small extent. The stretching vibrations of the type of the
bonds mentioned above appear within a region which is
characteristic for these specific bonds. As shown in Figure
1 these frequencies appear in the range of approximately
3600 cm^{-1} to 1500 cm^{-1}. The intensity of an infrared absorp-
tion band depends on the disturbance of the charge distri-
bution within the molecule caused by vibration. A large
change in this charge distribution will cause a stronger
absorption.

Various groups, such as the alcoholic hydrozyl group and carbonyl groups, have absorption bands which appear within a range characteristic of a specific group and serve to identify that group. These absorption bands are called "characteristic frequencies" or "characteristic absorption bands." In the past two decades, a considerable body of data concerning these "characteristic absorption bands" has been accumulated (1, 2, 7, 9, 12, 16, 18, 33).

Absorption bands due to the stretching of single bonds such as, C-O, C-C, C-N, C- halogen, and also bands due to bending vibrations of various bonds appear in a region below 1600 cm^{-1} (Figure 1). This lower frequency range of infrared spectrum, namely, the region between approximately 1300 to 650 cm^{-1} is referred to as the "finger-print region." In this region of infrared spectrum each compound has a pattern specific to itself. This unique feature of infrared spectroscopy provides an excellent tool for qualitative measurement of compounds.

Adsorbed Molecules and their Spectra

A molecule can become attached to a surface by either physical adsorption or chemisorption. Physical adsorption takes place through forces of attraction such as those causing the liquefaction of gases. Thus, in physical adsorption no electron transfer takes place. In chemisorption, however, the surface will tend to form chemical
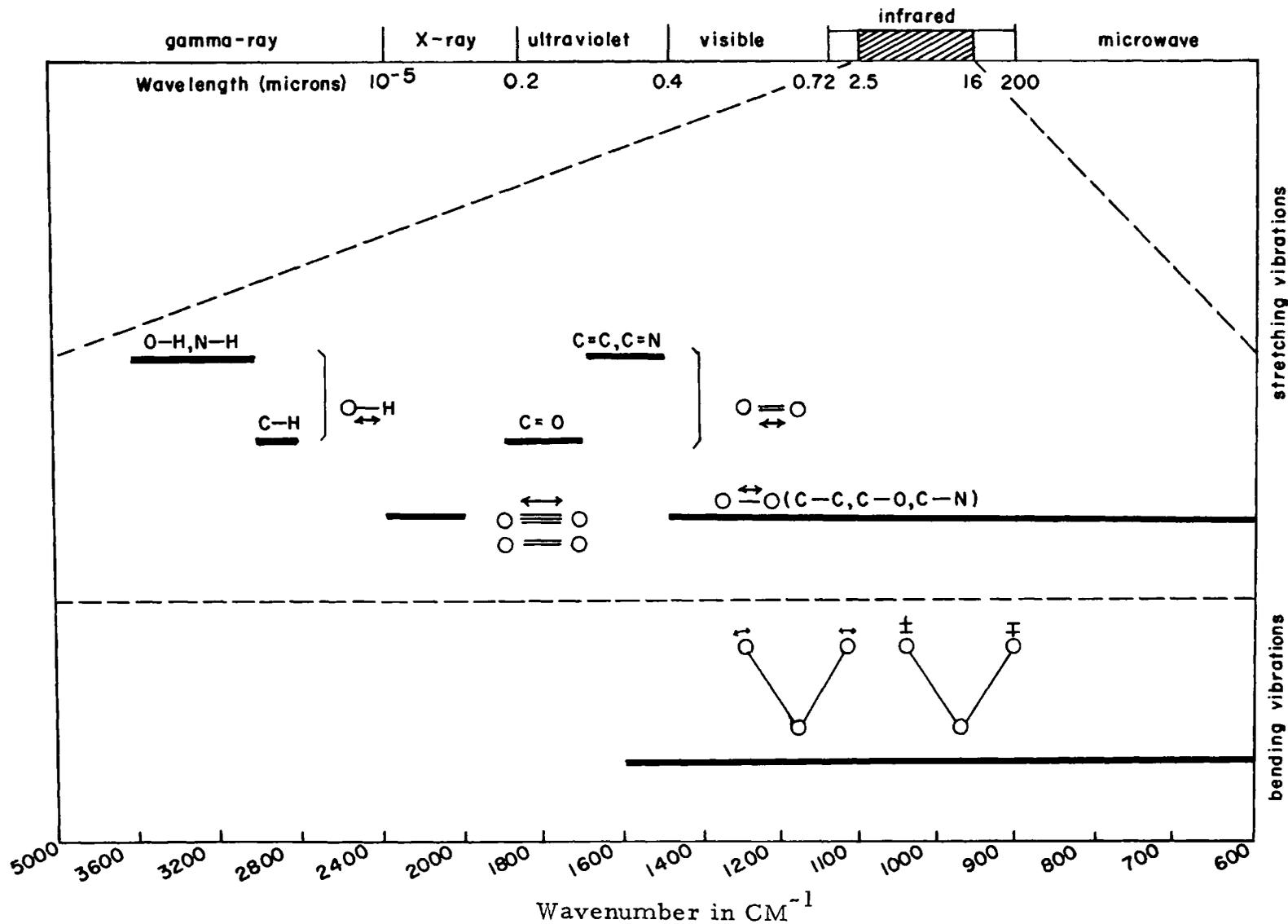
FIGURE 1 - BENDING AND STRETCHING VIBRATIONS

bonds with the adsorbed molecules. Thus, electron transfer may occur. In chemisorption, the adsorbed molecules may be formed by (12):

1. Dissociative adsorption, where a single bond in the reactant breaks into two adsorbed molecules.

2. Adsorption, which involves opening of a multiple bond.

3. Formation of a coordination bond between the reactant and the surface.

Spectra of physically adsorbed molecules resemble those of gaseous, liquid, or dissolved states. In some cases small differences in band positions have been observed during physical adsorption. However, the magnitude of these differences are the same as those observed between various unadsorbed states.

The infrared spectra of chemisorbed molecules are quite different from their spectra in unadsorbed states. Some of the bands of spectra are very similar, but differences appear when longer wavelengths are scanned. One criterion of chemisorption is the appearance of an infrared absorption band due to the formation of a chemical bond between the surface and the adsorbed molecules.

Spectra of unknown compounds are interpreted by comparing them with spectra of compounds of known structure. Since surface species formed by chemisorption do not have

exact equivalents among conventional compounds, problems have arisen in the interpretation of their spectra. However, the majority of these difficulties have been overcome and now the spectra of surface species can be interpreted with reasonable and self-consistant results.

III. EXPERIMENTAL EQUIPMENT

A glass vacuum system, attached to a mechanical pump and a diffusion pump, was employed to evacuate the gas cell used in this experiment. Liquid ethanol was vaporized by injecting a portion of it into a 50-mm double neck round bottom flask which was a part of the vacuum system. Gaseous ethanol was collected in the cell at various pressures, then the cell was transferred to a Beckman IR 4 infrared spectrophotometer for obtaining the spectra.

General Arrangement

The general arrangement of the equipment is shown in Figure 2. The main portion of the vacuum system was made of 1-in. OD Pyrex brand glass tubing approximately 27 inches long. High vacuum stopcocks were used to allow separation between different parts of the vacuum system. Other major parts of the vacuum system consisted of a Duo-Seal vacuum pump, a mercury diffusion pump, a 10 cm gas cell, two high vacuum gauges, and an absolute and differential manometer.

High vacuum rubber tubing was used to connect the mercury diffusion pump to the mechanical pump. The

LEGEND

1. Absolute and differential monometer
2. High vacuum tubing
3. Phillips gauge
4. Vacuum gauge control
5. Ice chest
6. Copper coil
7. Injection flask
8. Air drier
9. 10 cm. gas cell
10. Water trap
11. Variac
12. Voltmeter
13. High vacuum pump
14. Mercury diffusion pump
15. Cooling jacket
16. Heating coil
17. Pressure gauge
18. 1" O.D. glass tubing
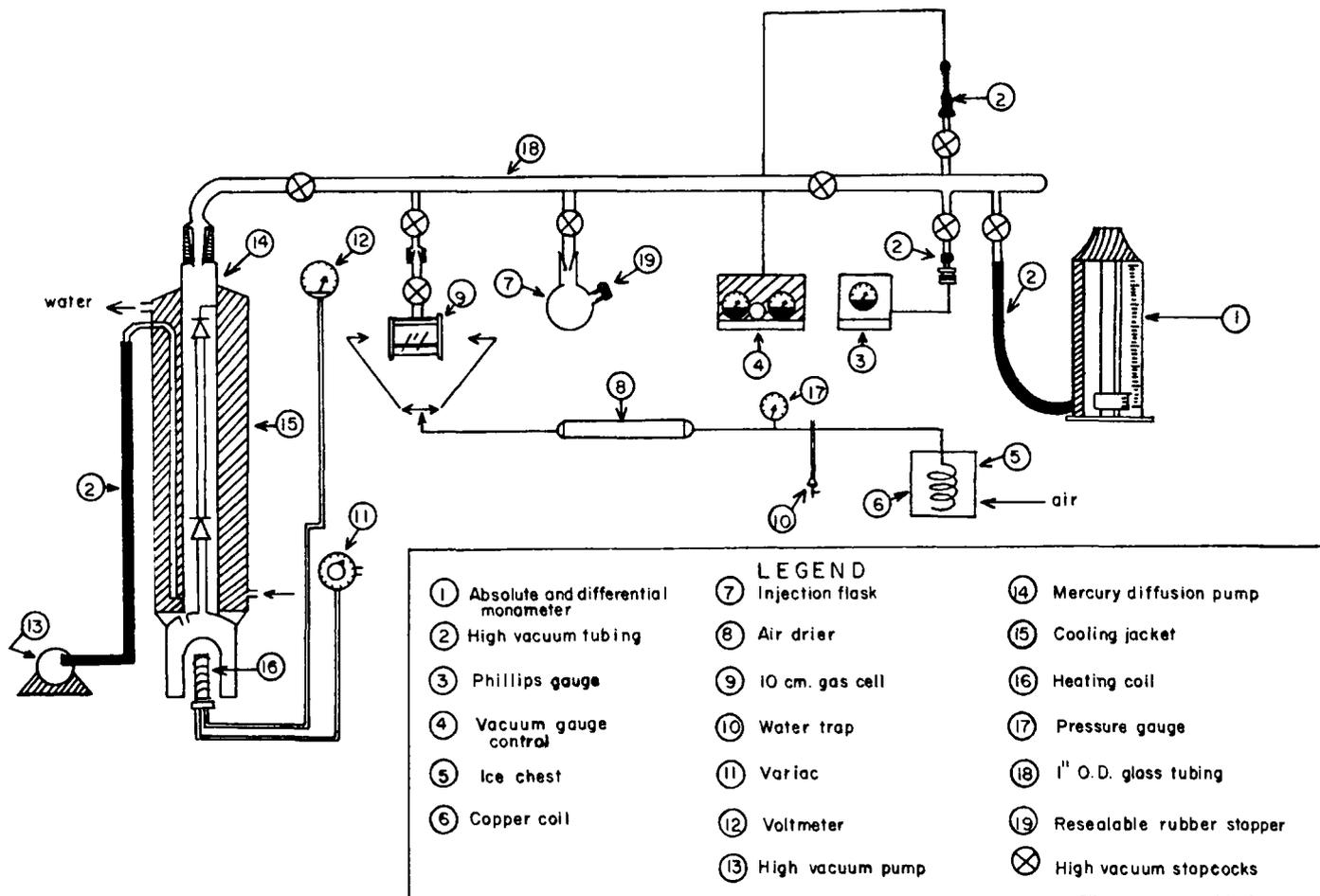19. Resealable rubber stopper
⊗ High vacuum stopcocks

FIGURE 2 - SCHEMATIC DRAWING OF THE APPARATUS

manometer and the high vacuum gauges were also connected to the system by means of high vacuum rubber tubing.

A variac was employed to control the amount of current passing through the heater in the diffusion pump. The voltage across the heater was read from an AC voltmeter.

Liquid ethanol was furnished to the vacuum system by means of a hypodermic syringe. The liquid was injected through a serum vial stopper into the double neck round bottom flask. The liquid ethanol was vaporized by creating a differential pressure between the round bottom flask and the rest of the vacuum system.

During the course of the experiment, whenever the gas cell was heated the cell windows were cooled by a stream of dry air. Laboratory compressed air was first passed through a copper coil immersed in ice water and the condensed water was collected in a water trap. The air was then passed through a 2" OD 60-inch long glass column containing calcium chloride.

Vacuum Pump

The vacuum pump used in this study was a Welch Duo-Seal Model 1402 B, which was manufactured by the Welch Scientific Company, Chicago, Illinois. The pump was a rotary type with two-stages. This model was provided with a vented exhaust which minimized the condensation of vapors in the compression cycle of the exhaust stage by introducing

an adjustable flow of atmospheric air. The admitted air lowered the partial pressure of the vapor below its saturation pressure. This prevented condensation and the vapors were expelled with the exhaust gases. The pump had an oil capacity of 2200 milliliters and an approximate pumping speed of 525 RPM. Under the best operational conditions the pump could produce an ultimate pressure of $1x10^{-4}$ millimeters.

Diffusion Pump

High vacuum was obtained by a two-stage mercury diffusion pump manufactured by the Western Scientific Appliances Company, Berkeley, California.

The forepump line passed through the condenser to eliminate the danger of mercury passing into the mechanical pump. Condensed mercury was returned to the boiler by an internal trapping tube. The interior of the pump was a 41-mm tube which provided a large annular jet area and hence an extremely fast pumping action.

The diffusion pump had a 115-volt heater in the boiler. A variac was used to adjust the current to 60-65 volts as recommended by the manufacturer.

In conjunction with dry ice this diffusion pump could produce a vacuum of $1x10^{-7}$ millimeters.

Gas Cell

The gas cell used in this experiment is illustrated in Figure 3. It was a ten centimeter fixed-path gas cell manufactured by the Beckman Instruments, Inc., Scientific and Process Division, Fullerton, California. The cell was designed to be used with all Beckman infrared spectrophoto-meters.

The gas cell was equipped with a single filling tube with stopcock for sample introduction. The cell had sodium chloride windows. The windows were attached to the glass body of the cell by means of lead gaskets which had been amalgamated with mercury to form a gas-tight seal between the body and the windows. The design of the cell allowed it to be used in the pressure range of zero to 800 milli-meters.

Vacuum Gauge Control

In this research the pressure range of 5 to 1000 microns was measured by a vacuum gauge control type 701; manufactured by the NRC Equipment Corporation, Newton, Mass. The gauge was a thermocouple vacuum gauge with a range of 1 to 1000 microns of mercury. The instrument operated on a normal 115 volt power source. The gauge operated on the principle that the rate at which heat is
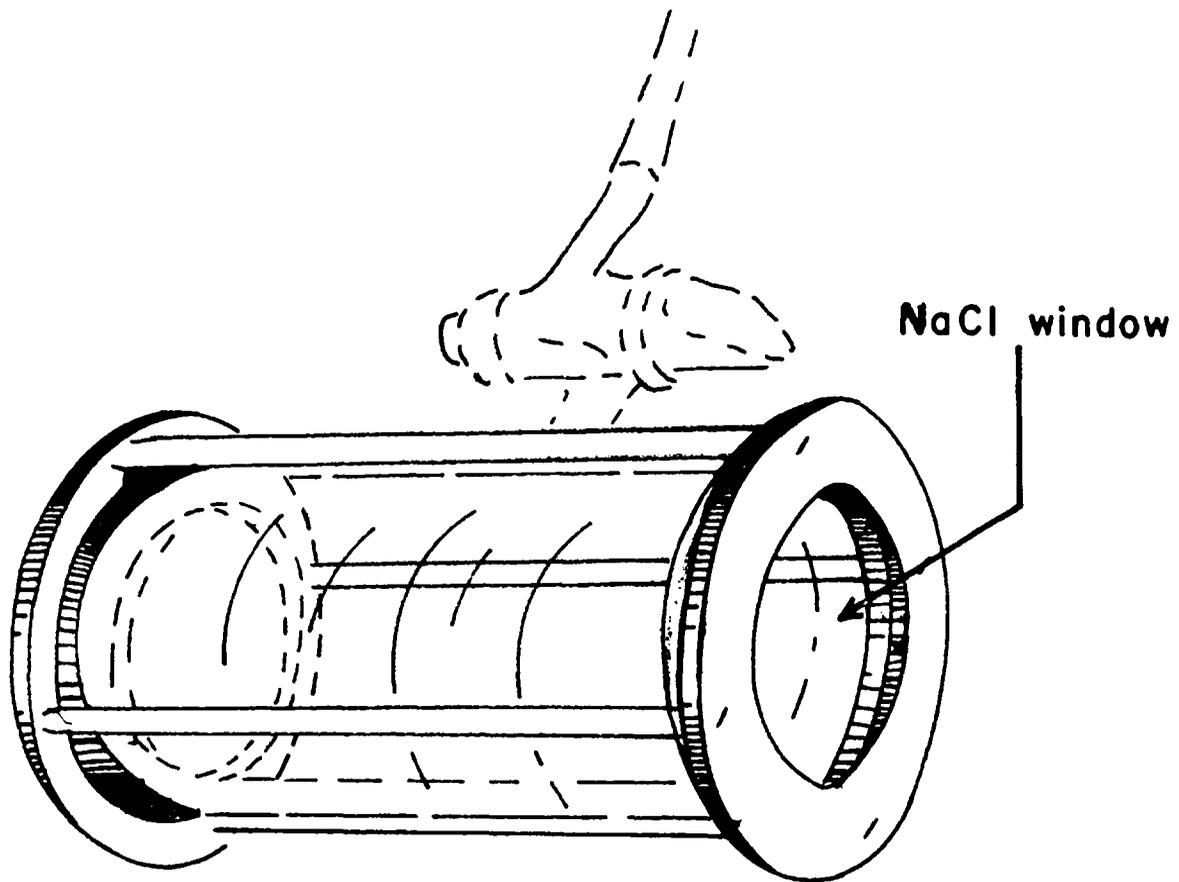
NaCl window

FIGURE 3 - TEN CENTIMETER FIXED-PATH GAS CELL

removed from a filament carrying a constant current is a function of the pressure of the gas surrounding it.

Philips Gauge

A Philips Gauge type PHG-1 was used to measure the pressures below 5 microns. This was a cold cathode type ionization gauge manufactured by the Consolidated Vacuum Corporation, Pasadena, California. It covered the range 0.01 to 25 microns Hg and measured total pressures, including condensable vapors. This gauge was provided with a microammeter with two scales. The two scales covered the ranges from 0.01 to 0.1 microns Hg and 0.1 to 25 microns mercury. A two position switch was used to select the desired scale. The gauge operated on a 115-volt, 60-cycle power supply.

The principle employed was the measurement of an ion current produced by a high voltage discharge. In the Philips Gauge tube the electrons were emitted by the cathode spiral as they move across the magnetic field. This action of the electrons increases the chance of them colliding with the gas molecules present, produces greater intensity, and keeps up the glow discharge.

Absolute and Differential Manometer

An absolute and differential manometer was used to measure the pressures above 1.0 millimeters. This manometer

was manufactured by the Manostat Corporation, New York, N. Y., and, as the name implies, the manometer was designed to measure either absolute or differential pressure. Both top and bottom ends of the manometer were open. If used as a differential manometer, the opening on the top would be connected to the system and the opening at the bottom would be left open to the atmosphere. The pressure reading would be obtained by subtracting the height of the mercury in the column from the atmospheric pressure (760 mm at 0°C). However, if an absolute pressure reading were desired the manometer would be tilted, with both ends open, until the entire column were filled with mercury, then the opening on the top would be closed and the manometer returned to its normal position. The opening at the bottom would then be connected to the system and pressure readings obtained by measuring the height of the mercury in the column. In both uses of the manometer the pressure to be measured would have to be below atmospheric pressure. In this study the manometer was connected so that absolute pressure readings were obtained.

IR 4 Infrared Spectrophotometer

The spectrophotometer used in this study was an IR 4 infrared recording spectrophotometer, manufactured by the Beckman Instruments, Inc., Fullerton, California. The Beckman IR 4 was a double beam instrument which was

designed for qualitative, quantitative, and structural analysis. It had double beam optical null, single beam amplifier, a double monochromator and a strip chart recorder.

The wavelength range, when sodium chloride prisms are used, was continuous from 1 to 16 microns. The IR 4 had a push button controlled wavelength scanning system which automatically indexed the scan to start at 15 microns, interrupted scanning at 1 micron, and returned to the starting wavelength with the chart in registry, ready for the next run. The spectra were recorded in terms of per cent transmittance, absorbance, or energy versus wavelength.

The Beckman IR 4 was provided with four interlocking push button switches to control the scanning rate of the wavelength device system. These switches provide 8 different scanning rates which range from 0.02 microns per minute to 5.0 microns per minute. In this study a scanning speed of 0.2 microns per minute was employed for all analyses.

The instrument was also equipped with a slit dial which gave a continous indication of the machine slit width. The range was from zero to 3.0 millimeters. The slit dial at the beginning of each run was set at 0.75 mm and 1000 cm^{-1}. Then the wavelength gear was engaged and the wavenumber was set at 720 cm^{-1} by turning the manual wavelength control.

The Beckman IR 4 was used as a double beam instrument with sodium chloride prisms. The gas cell was placed in the sample beam and air was used as the reference.

Heat Source and Temperature Measurement

Three infrared heating lamps were used to heat the gas cell when it was necessary. In order for the gas cell to be heated uniformly the heating lamps were placed radially, about the cell axis, at 120° angle from each other.

A mercury immersion type thermometer was used to determine the approximate temperature of the gas cell. To obtain a reading, the thermometer was attached to the outside of the glass part of the cell.

Hydrogen Purifier

Hydrogenation of the surface species was attempted to determine if the C-C bond of the ethanol had been ruptured. The hydrogen gas was purified before it was introduced into the system. Purification was accomplished by using a catalytic purifier for electrolytic hydrogen, manufactured by the Engelhard Industries, Inc., Newark, N. J.

Materials

The lithium fluoride crystals used in this research were optical grade (on the order of 1 PPM impurities) crystals from the Harshaw Chemical Company, Crystal-Solid Division, Cleveland, Ohio. These crystals were obtained in the form of "random cuttings," measuring 8 to 20 millimeters.

The ethyl alcohol was supplied by the U. S. Industrial Chemicals Company, Division of National Distribution and Chemicals Corporation, New York, N. Y. It was absolute ethanol, reagent quality, and was used without further purification.

The hydrogen used in this study was C P grade and supplied by Dye-Oxygen Company, Tucson, Arizona. Hydrogen was passed through the hydrogen purifier before it was used.

IV. EXPERIMENTAL PROCEDURE

The experimental work in this study consisted essentially of treating lithium flouride crystals in various ways, placing the crystals in the gas cell, exposing them to ethanol vapor, and obtaining the spectra of the adsorbed species.

The Beckman IR 4 spectrophotometer used in this experiment was always left in stand by position, so there was no need to allow for a warm up period. During the entire course of this experiment the operation of the IR 4 was standardized so that all variables such as scanning speed, slit width and gain were constant.

Prior to each run the gas cell was evacuated for 24 hours, then after the background spectrum was obtained, ethanol vapor at 50 mm was introduced into the cell. A spectrum at this pressure was recorded. Next by stepwise reduction of the gas pressure in the cell the spectra at 30 mm, 20 mm, 10 mm, 5 mm, 1 mm, 200 microns, and 100 microns were also obtained. All the spectra were recorded at 20°C.

A preliminary experiment was performed to obtain the spectra of ethanol vapor alone at various pressures. These spectra were obtained to be compared with those recorded later in the presence of LiF crystals.

Optical grade LiF crystals were used. These crystals were exposed to ethanol vapor in two forms:

1. Cleaved pieces of crystals with smooth surfaces.

2. Pieces which were bent after cleavage.

In either case 10 pieces of crystals measuring approximately 1x10x15 mm were arranged in a row and placed inside the gas cell. In each case, after introduction of ethanol at 50 mm into the cell, the crystals were allowed to remain exposed to the vapor (at this pressure) for two hours.

Two experiments were performed using LiF in granular and powder form. The granular LiF was prepared by grinding scraps from crystal cleavage in an agate mortar and pestle. Pieces measuring approximately 1x2x2 mm were then separated and placed in the gas cell. The LiF powder was about 100 mesh, and was prepared from the scraps in the same way as the granular LiF. In both of the experiments the LiF was exposed to ethanol vapor (50 mm) for two hours before any spectra were recorded.

Cleavage Procedure

The LiF crystal structure is face centered cubic, with (110) glide planes and (100) cleavage planes. In this study the LiF crystals were cleaved so that only the normal (100) cleavage planes were exposed.

For cleaving the LiF crystals the procedure suggested by Hall (20) was followed. A small hammer with ball

head and several single-edge razor blades were used. In
some cases a wedge type barber's razor was used which
worked much better than a single-edge razor blade.

To cleave the crystals the cleavage chisel was
placed so that the crystal was bisected. Then a sharp tap
was applied on the chisel with the hammer. This caused
the crack to pass rapidly through the crystal, producing
flat, smooth faces on the cleaved crystals. Reference (21)
gives a more detailed treatment of this subject. After the
crystals were cleaved each measured approximately 1x10x15
millimeters.

In the last run of this experiment, bent LiF
crystals were used. These crystals were first cleaved
according to the above procedure and then placed between
two smooth surfaces one at a time and a compression force
was applied (by hand) along the longest axis until the
crystal was bent.

Crystal Arrangement

The general arrangement of the crystals on the
aluminum plate is shown in Figure 4. The crystals were
positioned in the gas cell by placing them in a row on
an aluminum plate. The plate was 8 cm. by 2.5 cm and had
a thickness of 3 millimeters. Narrow slits were made on
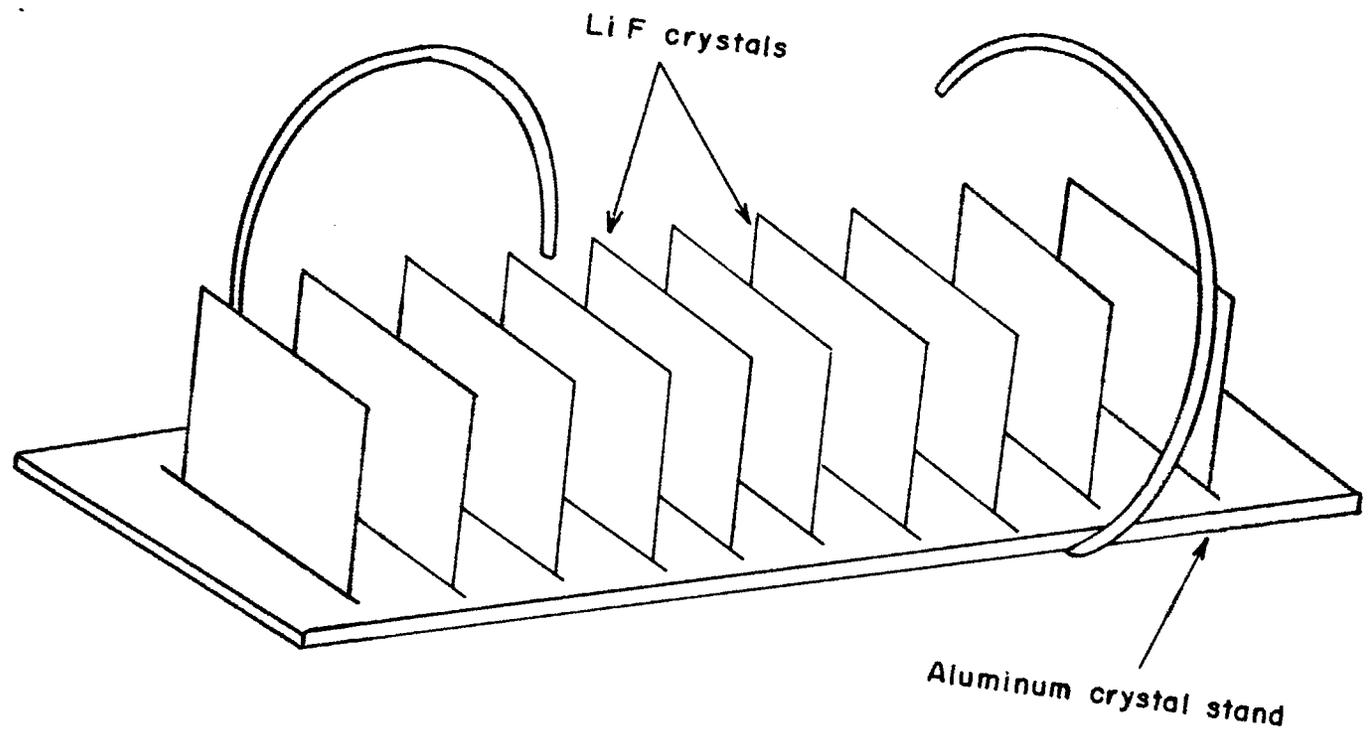the plate and the crystals were cemented in the slits

FIGURE 4 - ARRANGEMENT OF LiF CRYSTALS ON ALUMINUM STAND

using Duro epoxy, manufactured by Woodhill Chemical Company, Cleveland, Ohio.

Ten crystals of approximately the same size were used in each run. The arrangement of the crystals on the aluminum plate was such that ethanol vapor had easy access to the crystal surfaces. The plate itself was held in the cell by means of two pieces of brass wire shaped in the form of a semicircle.

To place the crystal set inside the cell, the cell had to be disassembled. This was done by removing the four screws from one of the end flanges and removing one of the windows. The detailed procedure on the assembly and disassembly of the cell was provided by the manufacturer (see experimental equipment, gas cell).

Evacuation Procedure

To start up the vacuum system, the mechanical pump was turned on and the system was allowed to reach a pressure of 500 microns. At this pressure the mercury diffusion pump was started. By means of the variac the current passing through the heater was adjusted so that the heater operated on 60 volts.

The ultimate vacuum obtained by this system was 0.5 microns (Philips Gauge). In the first run this vacuum was obtained after 13 hours of evacuation.

Whenever the gas cell was detached from the system, the stopcock just above the cell assembly (see Figure 2) was turned off in advance and the system remained under vacuum. During the entire course of this experiment the system was kept under vacuum.

When a vacuum higher than 0.5 microns was desired it was attained by using liquid nitrogen. A small round bottom flask was attached to the system (in place of the double neck injection flask, Figure 2). The system was evacuated for a long period of time (usually 10 hours), then the flask was immersed in liquid nitrogen. The central portion of the glass tubing which connected the cell to the round bottom flask was shut off from the rest of the system by closing the two stopcocks on each end of this portion. The flask remained immersed in the liquid nitrogen for at least 8 hours. In this way a vacuum of $2.2x10^{-6}$ microns was obtained (see calculation of pressure).

Heating Procedure

To heat the gas cell the three infrared heating lamps were positioned so that the cell would be heated uniformly. The estimated maximum temperature of the cell during the heat treatment was 120°C.

In order to avoid damage to the NaCl windows when the cell was being heated, dry cool air was blown on the

windows. This also prevented damage to the mercury seal between the windows and the glass-body.

Analysis Procedure

The Beckman IR 4 spectrophotometer used in this study was located in the Chemistry Building. Since the spectrophotometer was located in a different building, it was necessary to detach the cell from the vacuum system to obtain a spectrum. The time which elapsed between the detachment of the cell and the positioning of it in the spectrophotometer was about 10 minutes. After a spectrum was obtained the cell was reconnected to the system. The cell remained shut off from the rest of the system until the small portion of the glass tubing which was exposed to the air (due to the cell detachment) was evacuated. Usually it did not take more than 15 minutes for the system to reach the ultimate vacuum (0.5 microns); however, a period of 45 minutes to one hour was allowed before the cell was opened to the system.

Spectra of ethanol vapor at various pressures were obtained by evacuating the cell for 24 hours and then introducing ethanol at 50 mm into the cell. The spectrum of ethanol at this pressure was recorded. Then by stepwise reduction of the gas pressure in the cell, spectra at 30 mm, 20 mm, 10 mm, 5 mm, 1 mm, 200 microns,

and 100 microns were obtained. All the spectra were
recorded at 20 degrees centigrade.

With LiF crystals in the cell essentially the
same procedure, as in the case of ethanol vapor alone,
was followed. However, after ethanol at 50 mm was intro-
duced into the cell, the crystals remained exposed to the
vapor for a period of two hours. Then the first spectrum
was obtained (at 50 mm).

The hydrogenation of the surface species was
accomplished by introducing purified hydrogen at 60 mm
pressure into the cell, then the crystals remained exposed
to this gas for two hours. During the entire period of
hydrogenation, the cell was heated to about 120 degrees
centigrade. At the end of this period the heat was
removed and the cell was evacuated for 20 hours before
any spectrum was recorded.

Calculation of Pressure

In this study whenever liquid nitrogen was used
to obtain high vacuum, it was necessary to calculate the
pressure of the system (see evacuation procedure). One
of the correlations which is widely used to estimate the
vapor pressure in pure liquids is Clapeyron's equation
(24), which is usually written in the following form:

$$\frac{dp}{dT} = \frac{\Delta H}{T \Delta V} \, . \qquad\qquad (4\text{-}1)$$

If one of the phases is assumed to be a vapor behaving as an ideal gas and the molal volume of the denser phase is negligible in relation to the vapor phase, then equation (4-1) reduces to

$$\frac{d(\ln P)}{dT} = \frac{\Delta H}{RT^2} \, . \qquad\qquad (4\text{-}2)$$

If it is assumed that H is independent of temperature, then integration of equation (4-2) gives an equation of the following form for vapor pressures:

$$\ln P = \frac{A}{T} + B. \qquad\qquad (4\text{-}3)$$

Equation (4-3) was used in this study to estimate the pressure of the system. By using values for vapor pressure of ethanol at -31.3°C and -2.3°C the constants A and B were determined. Then the vapor pressure of ethanol at -31.3°C and -2.3°C the constants A and B were determined. Then the vapor pressure of ethanol at -195.7°C (liquid nitrogen temperature at 1.0 atm) was estimated, which gave the pressure of the system.

Since ethanol is a solid at such a low temperature (-195.7°C), the use of the above correlation is not quite suitable. However, only a rough estimate of the pressure was desired, so the use of this equation is conservative.

V. RESULTS

Preliminary experiments were performed to obtain the spectra of gaseous ethanol at different pressures for the purpose of comparing them with spectra obtained from later experiments using LiF crystals. Optical grade LiF crystals were used to determine which of the absorption bands ascribed to ethanol molecules become distorted by adsorption on these surfaces. Other experiments were performed to determine whether better results could be obtained.

Ethanol Vapor Spectra

The gas cell was evacuated for 24 hours, and the background spectrum of the evacuated cell was obtained. The spectra of ethanol vapor alone were then obtained at different pressures. The results for this part are presented in Figure 5. The spectra of ethanol vapor at higher pressures, namely 20, 30, and 50 mm, were also obtained. Since the difference between these spectra and the spectrum obtained at 10 mm appeared to be in the intensity of the bands, not in the resolution, these spectra at higher pressure are not shown in Figure 5. To establish the repeatability of these results a second
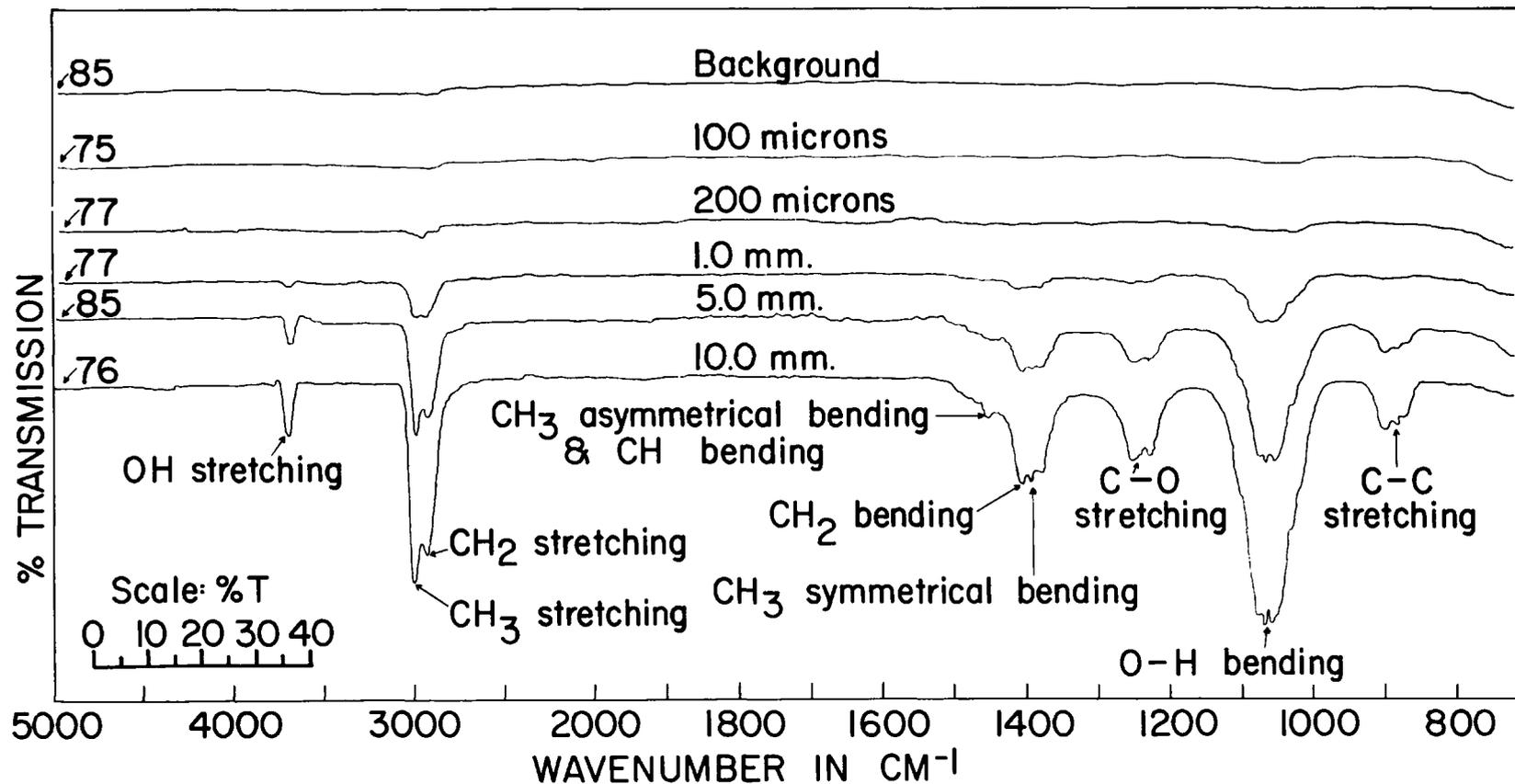
FIGURE 5 - INFRARED SPECTRA OF ETHANOL VAPOR AT 20°C.

experiment under the same conditions was performed. The results obtained were identical to those shown in Figure 5.

The infrared spectra of ethanol vapor shows absorption bands at 3700, 2990, 2920, 1460, 1410, 1385, 1250, 1075, 1060, 900, and 880 cm^{-1}. The absorption band appearing at 3700 cm^{-1} is assigned to the OH stretching vibrations (30). The bands at 2990 and 2920 cm^{-1} were assigned by Fox and Martin (18) to CH_3 and CH_2 stretching modes, respectively. Bellamy (10) has assigned the band at 1460 cm^{-1} to the CH_3 asymmetrical bending and CH_2 bending vibrations while the bands at 1410 and 1385 cm^{-1} were assigned to CH_2 bending and CH_3 bending modes, respectively. The bands which appear at 1250, and 1225 cm^{-1} are assigned to CO stretching frequencies (10). According to Zeiss and Tsutsui (34) the broad band near 1100 cm^{-1} which is resolved on the bottom with one peak at 1075 cm^{-1} and the other at 1060 cm^{-1} is assigned to OH bending modes. Finally the bands at 900 and 880 cm^{-1} are assigned to C-C stretching frequencies (26).

Adsorbed Ethanol Spectra

This part of the experiment consisted essentially of two runs. In the first run cleaved LiF crystals with smooth surfaces were arranged in the gas cell and then were exposed to ethanol vapor. In the second run, however, before placing the crystals in the cell they were bent in order to increase the dislocation density.

In the first run, after 24 hours of evacuation, the background spectrum of the cell with crystals was obtained. Then the crystals were exposed to ethanol at 50 mm and were kept at that condition for two hours. Spectra of the crystals exposed to ethanol vapor were recorded exactly at the same pressures as those used for ethanol vapor alone. The background spectrum and the spectra at various pressures obtained in this run are presented in Figure 6 (spectra at 20, 30, and 50 mm were recorded but not shown in this figure). A very small peak in the region of 2400 cm^{-1} is common to all the spectra. This is probably due to the $C = N$ bond of the epoxy resin used. As shown in Figure 6, when the pressure decreases, the absorption bands get smaller, and at a pressure of 200 microns, all the absorption bands due to ethanol disappear except for the two bands near 3000 cm^{-1}. The intensities of these bands are quite low. When the pressure of the cell is reduced to 100 microns, the situation stays practically the same (Figure 6). These bands appear at 2940, and 2860 cm^{-1} and are assigned to CH_3 and CH_2 stretching modes, respectively (18). A close comparison of these bands at 100 microns with those in the same vicinity at 10 mm shows that the band due to C-H stretching in the CH_3 group is shifted toward a longer wavelength, namely from 2990 cm^{-1} at 10 mm pressure to 2940 cm^{-1} at 100 microns. The band due to C-H stretching in CH_2 group is also shifted to a longer wavelength; in this case
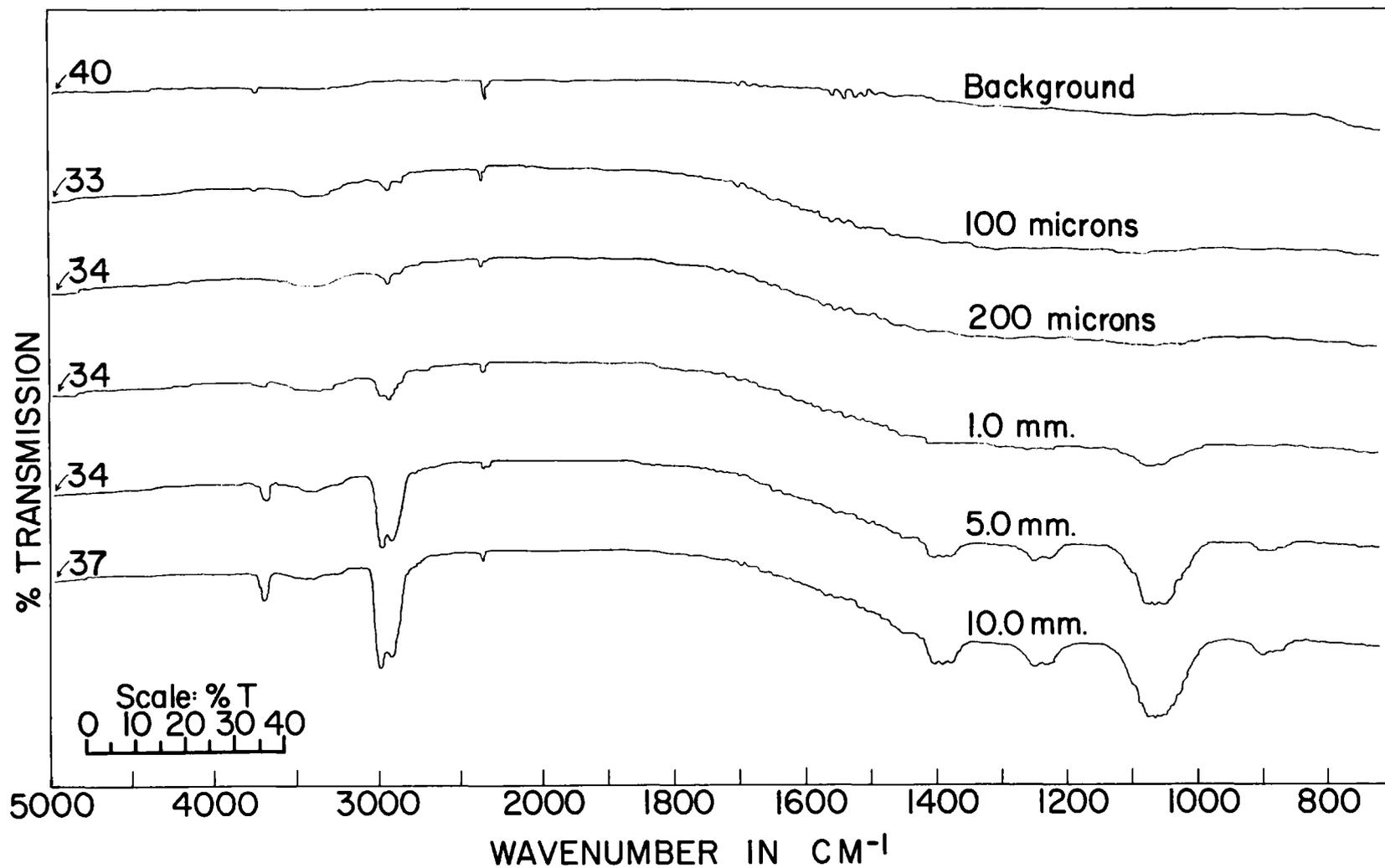
FIGURE 6 - INFRARED SPECTRA OF LiF CRYSTALS EXPOSED TO ETHANOL VAPOR AT 20°C.

the shift is from 2920 cm^{-1} at 10 mm to 2860 cm^{-1} at 100 microns. This shift of the bands did not occur until the other bands had disappeared. It should be mentioned here that at a pressure of 200 microns or lower, the bands due to CH_3 and CH_2 bending vibrations disappear completely.

After the pressure of the cell was reduced to 100 microns and the spectrum at this pressure was obtained, the cell was heated for three hours up to 120°C while being evacuated. At the end of this period the heat was removed and the cell was allowed to cool to room temperature while under vacuum. Spectrum B in Figure 7 was obtained after the above heat treatment. The bands at 2940 and 2860 cm^{-1} are much more pronounced and somewhat more separated than previous bands recorded at 100 microns (Figure 7). As shown by spectrum C, Figure 7, further heat treatment did not produce any changes in the intensities or positions of these absorption bands. To determine whether the C-C bond in the ethanol molecule was ruptured after the heat treatment, hydrogen gas at 60 mm was admitted to the cell; the crystals remained exposed to this gas at 120°C for 2 hours. Then after 23 hours of evacuation spectrum D in Figure 7 was obtained. The changes in the frequencies and characteristics of the bands in the vicinity of 3000 cm^{-1} are presented in Figure 8. Spectrum E shows the shift of these bands due to the adsorption and spectrum F indicates
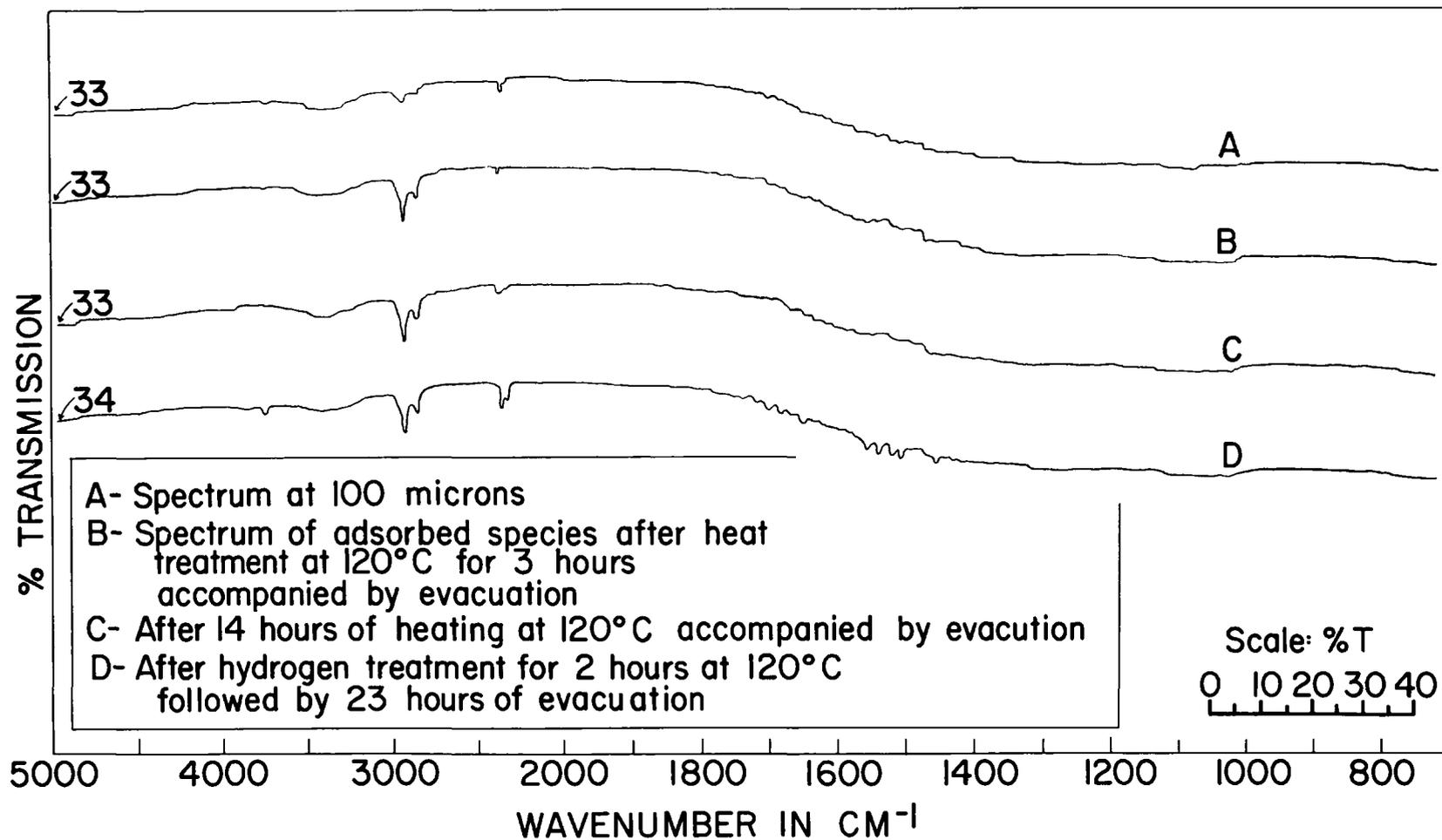
FIGURE 7 - INFRARED SPECTRA OF ADSORBED SPECIES ON LiF CRYSTALS AT VARIOUS CONDITIONS

The figure contains the following labels and legend:

% TRANSMISSION (vertical axis)

WAVENUMBER IN CM⁻¹ (horizontal axis): 5000, 4000, 3000, 2000, 1800, 1600, 1400, 1200, 1000, 800

Curve labels: A, B, C, D

Left-side values: 33, 33, 33, 34

Legend:
A- Spectrum at 100 microns
B- Spectrum of adsorbed species after heat treatment at 120°C for 3 hours accompanied by evacuation
C- After 14 hours of heating at 120°C accompanied by evacution
D- After hydrogen treatment for 2 hours at 120°C followed by 23 hours of evacuation

Scale: %T
0 10 20 30 40

FIGURE 8 - DEVELOPMENTAL STAGES OF THE INFRARED BAND
DUE TO ADSORBED SPECIES ON LiF CRYSTALS

the changes in the shape and intensity of the bands after heat treatment.

In the second run the crystals, as mentioned earlier, were bent prior to their placement in the cell. This run was performed to determine the effect of the dislocation density in the infrared absorption bands of the adsorbed molecules. It has been found that the dislocations 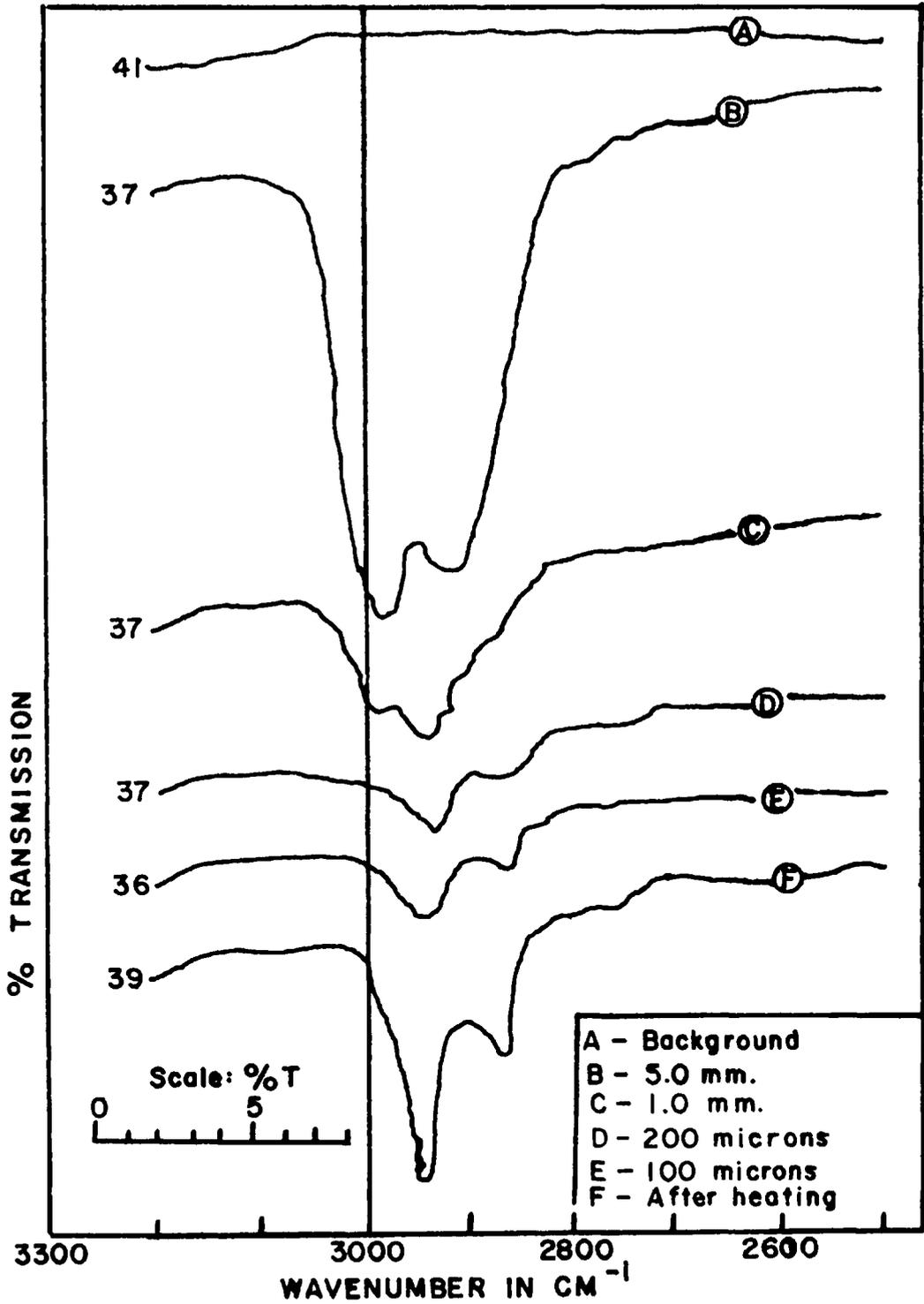in LiF crystals can be multiplied many fold by bending these crystals (19). If the dislocations are associated with adsorption, higher dislocation density in the crystals should cause more ethanol molecules to become adsorbed to the surface and consequently should result in higher intensity of the absorption bands.

After 24 hours of evacuation the background spectrum of the cell with crystals was obtained. After the crystals were exposed to ethanol vapor at 50 mm for 2 hours, the pressure of the gas inside the cell was reduced to 10 mm and a spectrum at this pressure was obtained. The spectra at 5.0 mm, 1.0 mm, 200 microns, and 100 microns were obtained by employing the exact procedure used in the first run. The results obtained for this part are presented in Figure 9. As in the first run all the absorption bands disappear at a pressure of 200 microns except for the two bands near 3000 cm^{-1}. A comparison between Figures 6 and 9 shows that the infrared bands near 3000 cm^{-1} (due to
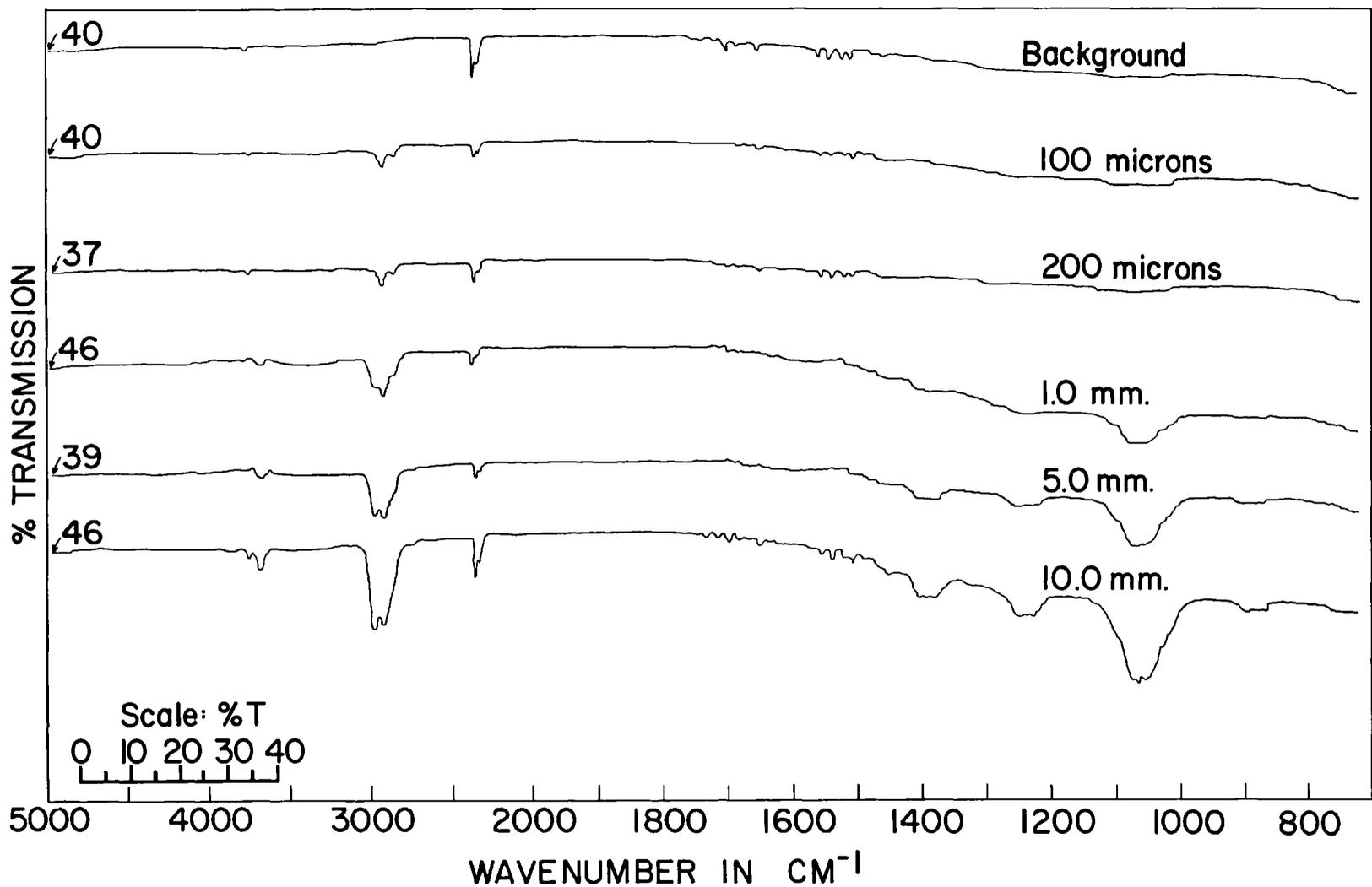
FIGURE 9 - INFRARED SPECTRA OF BENT LiF CRYSTALS EXPOSED TO ETHANOL VAPOR AT 20°C.

surface adsorption) at pressures of 200 or 100 microns have higher intensity when the crystals are bent.

In the first run no spectrum at pressures lower than 100 microns was obtained prior to the heat treatment. Thus, it was not determined whether the absorption bands appearing at 100 microns were due to physical adsorption or chemisorption. To determine the nature of the adsorption in this run after the spectrum at 100 microns was obtained, the cell was evacuated for eleven hours at a pressure of approximately 10^{-6} microns (using liquid nitrogen). Spectrum B in Figure 10 was obtained at the end of this period. As shown in the above spectrum the evacuation at the above pressure did not affect the intensity or the position of the adsorption bands near 3000 cm^{-1}. As indicated by spectrum C in Figure 10, further evacuation did not produce any change in the above absorption bands. After the cell was heated for three hours at 120°C and cooled to room temperature while under vacuum, spectrum D in Figure 10 was obtained. As in the first run the bands near 3000 cm^{-1} are separated and have higher intensity than those obtained before heat was applied.

Comparison of the spectrum at 10 mm pressure with that at 100 microns in Figure 9 shows that the bands near 3000 cm^{-1} are shifted to a longer wavelength region. The band assigned to C-H stretching in the CH_3 group shifts from 2980 cm^{-1} to 2950 cm^{-1}, and the absorption band
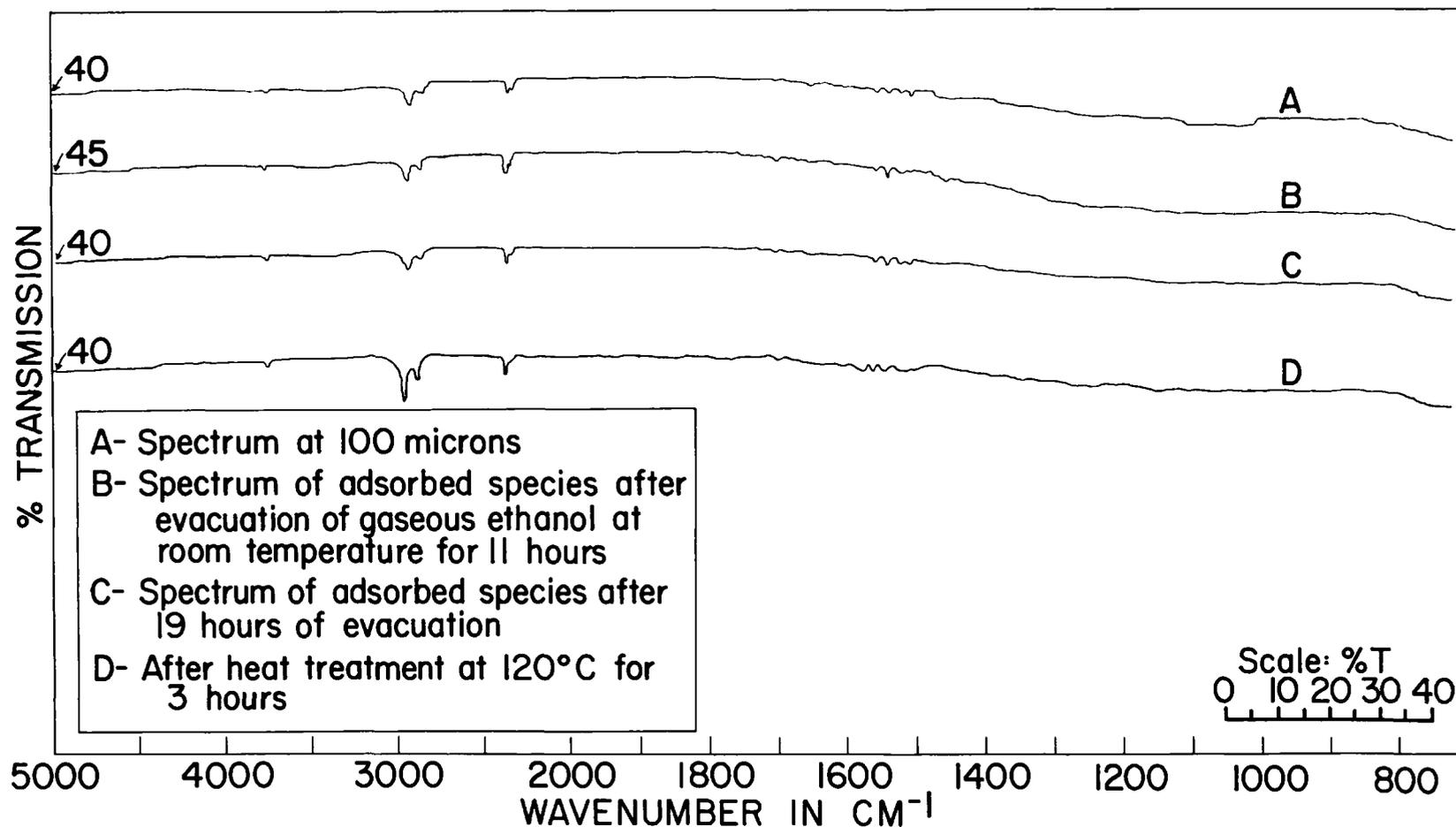
FIGURE 10 - INFRARED SPECTRA OF ADSORBED SPECIES ON BENT LiF CRYSTALS AT VARIOUS CONDITIONS

The figure contains the following legend:

A- Spectrum at 100 microns
B- Spectrum of adsorbed species after evacuation of gaseous ethanol at room temperature for 11 hours
C- Spectrum of adsorbed species after 19 hours of evacuation
D- After heat treatment at 120°C for 3 hours

Axis labels: % TRANSMISSION (vertical), WAVENUMBER IN CM⁻¹ (horizontal)

Scale: %T   0 10 20 30 40

assigned to C-H stretching in the CH_2 group is shifted from 2925 cm^{-1} to 2875 cm^{-1}. Figure 11 shows the shift in the absorption bands near 3000 cm^{-1} in a larger scale. It should be emphasized here that the shift did not occur until the other bands had disappeared completely.

Calculations were performed to determine the force constant of C-H bonds in CH_3 and CH_2 groups before and after the shift in the absorption bands. The purpose of these calculations was to show that the C-H bonds in ethanol molecules are stretched after surface adsorption occurs. The results of these calculations are presented in Table I. These calculations indicate that in the two cases observed in this study, the force constant, k, is smaller after adsorption. This shows that the equilibrium distance between carbon and hydrogen atoms increases after adsorption. It should be mentioned that these values are based on the simple harmonic oscillator model, and are presented here just to illustrate the difference between the force constant before and after adsorption.

Other Experiments

Since increase in the surface area would have led to a higher molecular adsorption and consequently spectra with higher intensities, attempts were made to perform experiments using LiF in powder and granular form. A small glass cell with NaCl windows was constructed and the top
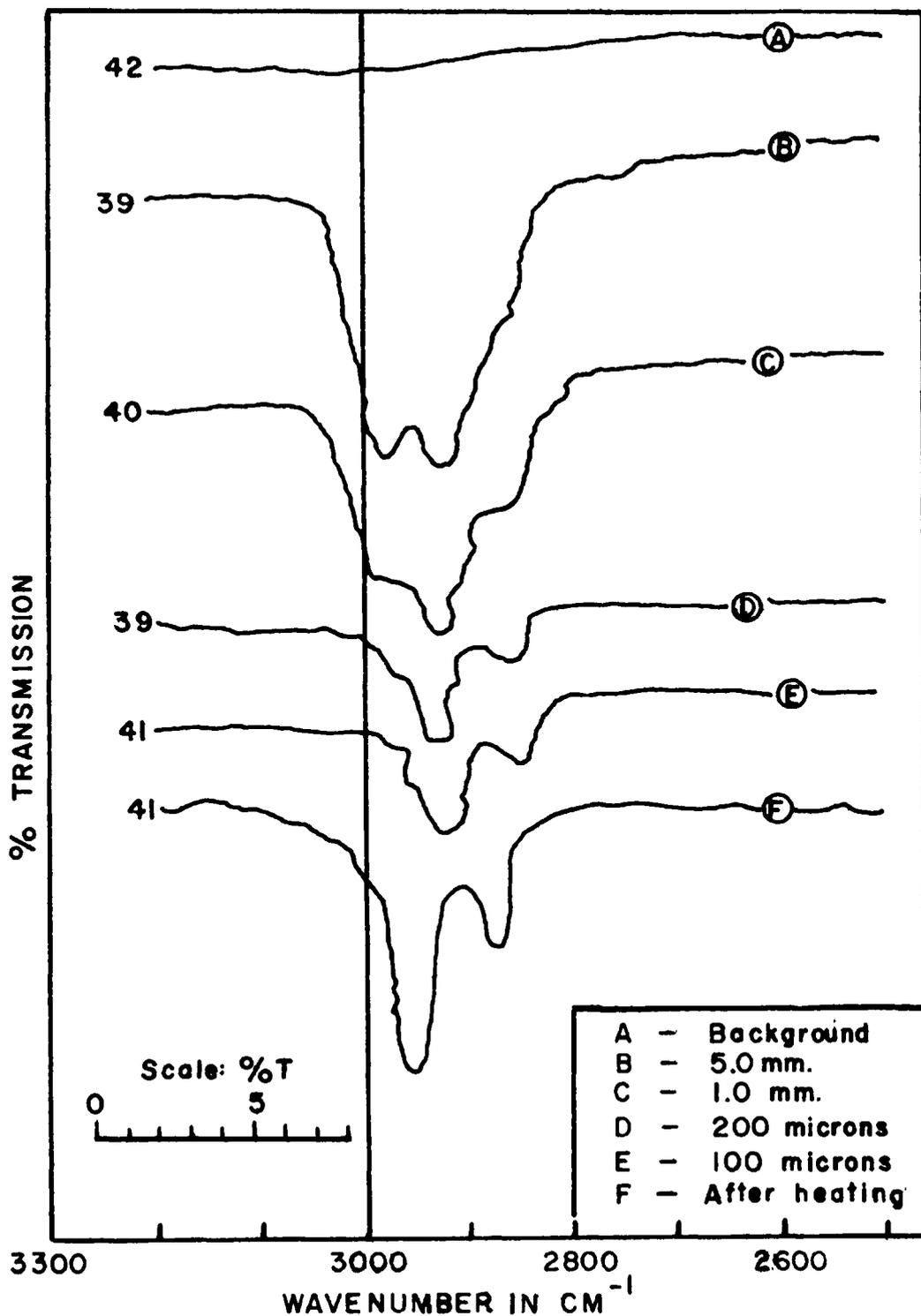
FIGURE 11 - DEVELOPMENTAL STAGES OF THE INFRARED BAND
DUE TO ADSORBED SPECIES ON BENT LiF CRYSTALS

Table I

Effect of Shift in IR Bands on Force Constant

	Force Constant, k, dynes per cm			
	Run 1		Run 2	
	CH_3	CH_2	CH_3	CH_2
Before Shift	5.24×10^5	5.02×10^5	5.22×10^5	5.02×10^5
After Shift	5.07×10^5	4.80×10^5	5.10×10^5	4.84×10^5

part of this cell was left open for the vapor to get in. This cell was mounted on a small piece of glass rod and held in the gas cell by means of two pieces of brass wire shaped in semicircular form.

The small cell was filled with 100 mesh lithium fluoride and was placed in the gas cell. After assemblage of the gas cell and proper evacuation, the cell was placed in the IR 4 spectrophotometer, but no transmission through the LiF powder was observed. When granular LiF was used, the percent transmission was quite low, and the spectra obtained did not provide any useful information.

VI. DISCUSSION

Comparison of the spectra shown in Figure 5 with those in Figure 6 indicates that the absorption bands near 3000 cm^{-1} at 100 microns (Figure 6) are definitely due to the adsorbed species. The fact that adsorption to the surface occurs was further confirmed by the presence of these bands after the cell had been evacuated for nineteen hours to a pressure of approximately 10^{-6} microns (spectrum C, Figure 10). Furthermore, presence of the absorption bands after evacuation of the cell at such a low pressure is a strong indication of the molecules being firmly attached to the surface. If the adsorption was physical, one would expect these bands to disappear at a vacuum of 10^{-6} microns. The fact that these adsorbed species withstand such a severe treatment is evidence for the occurance of the chemisorption process between the molecules and the surface.

In the spectra of adsorbed species (obtained after gaseous ethanol had been removed) the only observed bands are those due to CH_3 and CH_2 stretching. The bands due to the other vibrational modes, including those assigned to CH_3 and CH_2 bending frequencies, disappear. This indicates that the adsorbed molecules are oriented on the surface so that each molecule became more rigid. The disappearance

of these frequencies is also due to the fact that the number of C-H bonds involved is larger than the number of other bonds.

Spectra E and F in Figures 8 and 11 show the absorption bands due to adsorbed species before and after heat treatment. After heat is applied the bands become separated and have a much higher intensity. The behavior of these bands after heating can be interpreted in a number of ways, some of which can be ruled out due to the experimental evidence obtained in this study. One might assume that the attachment of the molecules to the surface before heating is due to physical adsorption, and after the heat treatment, chemical bonds between molecules and the surface are formed. The chemical bond formation brings about the higher intensity of the absorption bands. This possibility is ruled out because it was established earlier that the molecules were chemisorbed to the surface before heating. It is also logical to assume that when heat is applied the principal reaction of the ethanol with the surface is to break the C-C bonds, thereby producing two adsorbed species. This could very well change the intensity of the bands. However, this is also a false assumption since, after the hydrogenation process, the bands did not disappear, which indicated that the C-C bond had not been ruptured. The hydroxyl group in the ethanol molecule is highly polar and thus associates with any other molecule having some degree of

polar attraction. Therefore it is possible that the heat treatment caused the formation of the H-F bond which has characteristic absorption bands in the vicinity of 3000 cm^{-1}. If this were the case, however, other bands in the lower wavelength region should have developed from other vibrational and bending modes. The possibility that the crystal deformation in LiF due to heating caused the change in the absorption bands is quite remote, since LiF has a very stable structure at temperatures much higher that 120°C. The possibility that at elevated temperatures the surface reaction involved dehydrogenation of ethanol to produce acetaldehyde can easily be ruled out by the following:

1. Dehydrogenation of ethanol on LiF crystals at such a low temperature is extremely slow. Even at much higher temperatures such as 240 degrees centigrade the per cent conversion to acetaldehyde is quite small (21).

2. Formation of acetaldehyde on the surface should have given very strong absorption bands near 1740 and 1440 cm^{-1} (10). These bands were not observed.
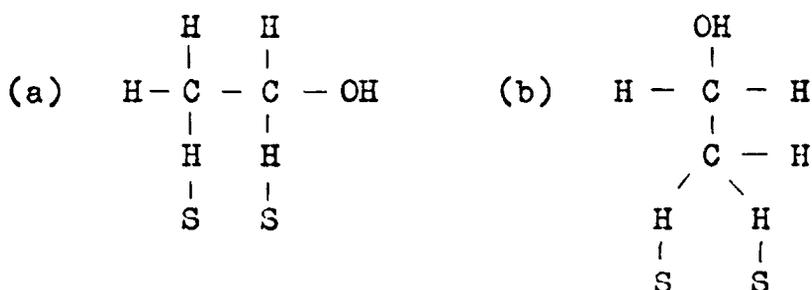
With the above possibilities ruled out, the following explanation seems quite logical. Application of heat produces a very small amount of mobility in the adsorbed molecules which allows the molecules to reorient themselves and occupy more favorable sites, thus stronger chemical

bonds between the surface and the molecules are formed which result in stronger infrared absorption bands. However, no experimental evidence obtained in this work can confirm this speculation.

The shift in the absorption bands is not due to the reduction of the gas pressure. Spectra shown in Figure 5 confirm this point, since no shift in the absorption bands is observed when the pressure is reduced. Examination of Figures 6 and 9 shows that the shift of the bands occur when other bands disappear. Thus the shift must be associated with the adsorbed molecules. This shift is observed in the bands ascribed to CH_3 and CH_2 stretching vibrations and is caused by the distortion in C-H bonds. The fact that these bands shift toward the longer wavelength region suggests that the equilibrium distance between carbon and hydrogen atoms increases due to the adsorption. The approximate calculation of the force constant, k, confirmed this point, since the values of k were smaller after adsorption. As shown in Figures 6 and 9 the only bands shifted are those due to CH_3 and CH_2 stretching modes; therefore, it is reasonable to conclude that only C-H bonds become distorted during the adsorption process.

Comparison between spectra E and F in Figure 8 with spectra E and F in Figure 11 shows that the increase in dislocation density (by bending crystals) results in higher surface adsorption.

Evidence gathered from this experimental work indicates that the attachment of the molecules to the surface is not due to dissociative adsorption. The only observable change which accompanied the adsorption process was the distortion of the C-H bonds in the CH_3 and CH_2 groups. This suggests that the adsorbed species have one or both of the following surface structures:

```
                H   H                        OH
                |   |                        |
    (a)     H – C – C – OH       (b)     H – C – H
                |   |                        |
                H   H                        C — H
                |   |                       / \
                S   S                      H   H
                                           |   |
                                           S   S
```

where, S, indicates the surface site. Structure (b) is easily ruled out since the relative intensity of the bands due to the CH_3 and CH_2 stretching did not change after adsorption or after heating. Moreover, a structure of this kind (structure b) would have caused a damping in C-H stretching frequency of either the CH_3 or CH_2 groups. With this possibility eliminated, ethanol molecules must be attached to the surface according to structure (a). The fact that these adsorbed molecules become quite firmly attached to the surface with only the C-H bonds becoming distorted indicates that the geometry of the surface (where adsorption takes place) is such that permits an attachment of this type. The dislocation is a strong candidate as

the surface site since there is a very strong electrostatic charge associated with it.

VII. CONCLUSIONS

The feasibility of applying infrared techniques
to the study of adsorbed species has been demonstrated.
By applying these techniques, useful qualitative informa-
tion was obtained.

Comparison of the spectra of ethanol vapor with
those recorded in the presence of LiF crystals indicates
that at room temperature ethanol molecules adsorb by form-
ing bonds with the surface. Due to the adsorption, the
infrared bands assigned to CH_3 and CH_2 stretching shift
toward longer wavelengths. This is caused by distortion
in the C-H bonds. Application of heat mobilizes the
adsorbed molecules toaa small extent. This mobility allows
the molecules to reorient themselves and occupy more favor-
able sites. The adsorption process does not involve disso-
ciation and consequently no new species are formed by this
process. Therefore, the following surface structure is
proposed for the adsorbed molecules:

```
        H    H
        |    |
  H  -  C  - C  - OH
        |    |
        H    H
        |    |
        S    S
```
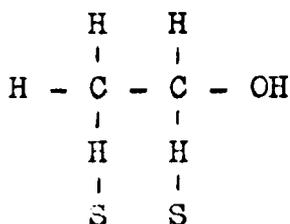
The adsorbed molecules become quite firmly attached to the
surface which produces a damping factor in some of the

vibrational modes. Therefore, the spectrum of the adsorbed species does not show all the vibrational bands due to the ethanol molecules. The increase of the dislocation density in the LiF crystals results in more adsorption. Comparison of Figures 8 and 11 makes this clear.

These findings support Hall's (21) work on the relation between dislocations and catalytic activity, but the orientation of the adsorbed molecule is not in complete harmony with the orientation which he speculated. The present work is rather more consistent with the two-point mechanism proposed by many investigators (1, 13, 23).

The strong coherence of ethanol molecules to the surface at room temperature leads to the conclusion that the crystal structure of LiF and the geometry of the ethanol molecules play an important role in the adsorption process.

NOMENCLATURE

A   constant

B.   constant

c   velocity of light

ΔH latent heat of vaporization

k   force constant

m   mass of vibrating atom

$\dfrac{dp}{dT}$ rate of change of vapor pressure with temperature

R   universal gas constant

v   potential energy

ΔV volume change accompanying the phase change of specific temperature

x   displacement of atoms from their equilibrium position

μ reduced mass of vibrating atoms

ν vibrational frequency in cm^{-1}

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