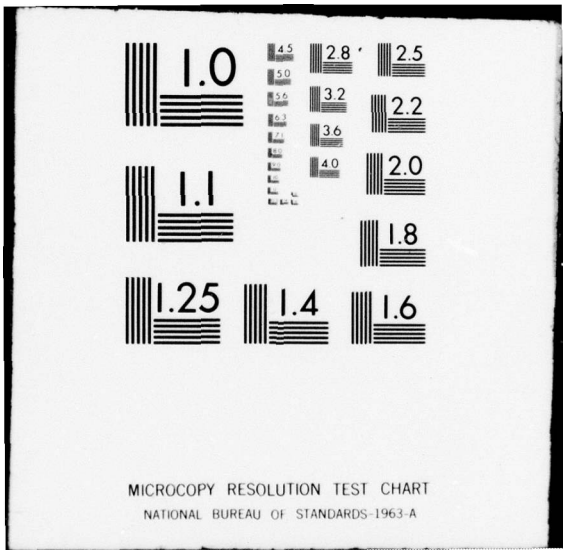
AD-A067 359 BATTELLE COLUMBUS LABS OHIO F/G 11/8
SOLIDIFICATION OF BOUNDARY LUBRICANT FILMS.(U)
DEC 78 E J DRAUGLIS, R J JAKOBSEN F33615-77-C-2026
UNCLASSIFIED AFAPL-TR-78-111 NL

1 OF 2
AD A067359


1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0
5.6
6.3
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AFAPL-TR-78-111

(2)

LEVEL II

AD A067359

DDC FILE COPY

SOLIDIFICATION OF BOUNDARY LUBRICANT FILMS

E. DRAUGLIS
R. J. JAKOBSEN

BATTELLE
COLUMBUS LABORATORIES
505 KING AVENUE
COLUMBUS, OHIO 43201

DECEMBER 1978

TECHNICAL REPORT AFAPL-TR-78-111
Final Report – APRIL 1977 – OCTOBER 1978

AIR FORCE AERO PROPULSION LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

Hoover A. Smith

HOOVER A. SMITH
Project Engineer

Howard F. Jones

HOWARD F. JONES
Chief, Lubrication Branch
Fuels and Lubrication Division

FOR THE COMMANDER

B. C. Dunnam

BLACKWELL C. DUNNAM
Chief, Fuels and Lubrication Division

"If your address has changed, if you wish to be removed from our mailing list, or if the addressee is no longer employed by your organization please notify AFAPL/SFL *,W-PAFB, OH 45433 to help us maintain a current mailing list".*

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

AIR FORCE/56780/22 March 1979 — 225

79-12
AD67359

DEPARTMENT OF THE AIR FORCE
AIR FORCE AERO PROPULSION LABORATORY (AFSC)
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

REPLY TO ATTN OF: SFL

25 Apr 79

SUBJECT: Correction of Final Report Date; AFAPL-TR-78-111

TO: DDC/TCA
Cameron Station
Alexandria VA 22314

1. The following corrections have been made to report AFAPL-TR-78-111, "Solidification of Boundary Lubricant Films."

a. Front cover: Final report date is Apr 77 to Oct 78

b. DD Form 1473, Block 5: Final report date is 15 Apr 77 to 15 Oct 78

2. Please note these corrections on your copy/copies of this report.

H. A. Smith
H. A. SMITH
Lubrication Branch
Fuels & Lubrication Division

AMERICAN REVOLUTION BICENTENNIAL 1776-1976

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: AFAPL-TR-78-111	2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle): SOLIDIFICATION OF BOUNDARY LUBRICANT FILMS.	5. TYPE OF REPORT & PERIOD COVERED: Final Technical Report. APR 77 - OCT 78,
6. PERFORMING ORG. REPORT NUMBER	
7. AUTHOR(s): E. J. Drauglis and R. J. Jakobsen	8. CONTRACT OR GRANT NUMBER(s): F33615-77-C-2026
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Battelle Columbus Laboratories, 505 King Avenue, Columbus, Ohio 43201	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: Project 2303, Task 2303S3, Work Unit 2303S302
11. CONTROLLING OFFICE NAME AND ADDRESS: Air Force Aero Propulsion Laboratory (SFL), Wright-Patterson Air Force Base, Ohio 45433	12. REPORT DATE: December 1978
	13. NUMBER OF PAGES: 96
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): Unclassified
	15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited

61102F

2303 S3

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

High pressure
Lubricants
Straight-chain alkanes
Diamond anvil cell
Fourier Transform Infrared Spectroscopy
Phase changes
Solidification

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

In this research lauric acid, dodecane, solutions of lauric acid in dodecane and a diester E-105 have been studied in a diamond window high pressure cell. Melting and crystallization behavior were studied as functions of pressure, temperature, time, and solution composition, by means of visual microscopic observation and Fourier Transform infrared spectroscopy. Of greatest immediate significance with respect to the development of improved lubricating fluids, are the experiments in which chemical reactions at a

(Continued) over

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. ABSTRACT (Continued)

simulated bearing surface were studied by coating the diamond windows with a thin layer of iron. In these experiments the formation of an iron salt of lauric acid was followed by infrared spectroscopy. This work demonstrates conclusively the power of this new experimental technique for studying chemical reactions at interfaces not only of model lubricants but also lubricants and additives of practical interest.

PREFACE

This technical report was prepared by the Chemistry Department of the Columbus Laboratories of the Battelle Memorial Institute. The work described herein was sponsored by the Air Force Aero Propulsion Laboratory (AFAPL), Air Force Systems Command, Wright-Patterson AFB, Ohio, under contract No. F33615-77-C-2026 for the period 15 April 1977 to 15 October 1978. This work was accomplished under Project 2303, Task 2303S3, Work Unit No. 2303S302.

At the beginning of the program Mr. C. M. Allen was principal investigator. Upon Mr. Allen's retirement on 1 October 1977, Dr. E. Drauglis became principal investigator. Mr. R. J. Jakobsen was reponsible for the infrared spectroscopy data. Mr. C. J. Riggle also made substantial technical contributions to the work.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

LIST OF TABLES

SUMMARY

In this research lauric acid, dodecane, solutions of lauric acid in dodecane and a diester E-105 have been studied in a diamond window high pressure cell. Melting and crystallization behavior were studied as functions of pressure, temperature, time, and solution composition, by means of visual microscopic observation and Fourier transform infrared spectroscopy. Of greatest immediate significance with respect to the development of improved lubricating fluids, are the experiments in which chemical reactions at a simulated bearing surface were studied by coating the diamond windows with a thin layer of iron. In these experiments the formation of an iron salt of lauric acid was followed by infrared spectroscopy. This work demonstrates conclusively the power of this new experimental technique for studying chemical reactions at interfaces not only of model lubricants but also lubricants and additives of practical interest.

In experiments performed in a non-metalized diamond cell, dodecane and lauric acid-dodecane solutions were found to crystallize over a pressure range of approximately 4 kbar. The crystallization pressure did not vary to a measurable degree with solution concentration but showed the expected increase with increasing temperature. However, the most concentrated solution (10 percent by weight) exhibited individual crystallization of first the lauric acid and then the dodecane within the pressure range.

The melting behavior of the lauric acid-dodecane solutions did show a dependence on lauric acid concentration. With decreasing pressures, 1 percent solutions gave no indication of partial melting or loss of long-range order until the solution melted sharply at about 2 kbar. On the other hand, 5 percent solutions showed signs of partial melting and loss of long-range order with total melting occurring at about 3 kbar. In the case of the 10 percent solutions, partial melting of dodecane was observed in the 10 to 5 kbar range, followed by the melting of the lauric acid. By the time the pressure was lowered to 4 kbar, both components had completely melted. The 10 percent solution did not show any long-range order in the solid state although some order was observed in the solid 1 percent and 5 percent solutions and in solid dodecane.

Studies of a 10 percent lauric acid-dodecane solutions at constant pressure showed marked spectral changes with time before solidification could be observed visually. These spectral changes are similar to those observed in the crystallization of lauric acid and indicate aggregation of lauric acid in the solution. Some time after these changes were observed, the lauric acid was observed to crystallize and later the dodecane solidified. This study indicates that aggregation of lauric acid in solution is similar to the formation of crystallites. Studies were also made of a diester E-105 (diethylhexyl adipate) and 1 percent solutions of tricresyl phosphate in E-105. No crystallization was observed even at pressures up to 20 kbar.

Preliminary experiments on 10 percent lauric acid-dodecane solutions in a diamond cell with iron-coated windows showed that a chemical reaction occurs between the iron and the lauric acid which results in the formation of iron laurate. This was demonstrated spectroscopically by observing that the intensity of the acid C=O band decreased with time as a new band characteristic of COO- vibrations in a carboxylate group appeared. Eventually the acid C=O band disappeared totally indicating that all of the lauric acid had reacted. The final intensity of the carboxylate band indicated the formation of an iron laurate film of thickness greater than a monolayer. These preliminary experiments show that the use of Fourier transform infrared spectroscopy on systems contained in a metalized diamond cell is a technique of great potential for studying chemical reactions at interfaces as a function of pressure, temperature and composition. In particular, the technique offers exciting new possibilities into obtaining a fundamental understanding of the mechanism by which lubricant additives help to form protective films.

SECTION I

INTRODUCTION

To better meet the lubricant requirements for future aero-propulsion systems, the Aero Propulsion Laboratory some time ago supported a program at Battelle's Columbus Laboratories (BCL) which was aimed at developing a more fundamental understanding of the physics and chemistry of boundary lubrication.[1] The basic working hypothesis of this program was that boundary lubrication must be attributed to relatively thick films (as much as hundreds of angstroms thick) having chemical and physical properties significantly different from those of the bulk fluid. The anomalous properties of these so-called boundary films could be shown to be due to the presence of a high degree of long-range order[1,2].

In order to test this hypothesis, Battelle workers devoted a great deal of effort to the development of techniques for the study of structure and order in boundary films. Success was obtained with a technique based on attenuated total reflection infrared spectroscopy with polarized radiation. In this technique the film to be investigated is deposited on an iron-coated germanium prism. Polarized infrared radiation is then transmitted through the prism, undergoing many reflections and interactions with the film. Spectra are obtained for several orientations of the polarization plane. By measuring and comparing the intensities of the various bands at different polarizations, one can determine the degree of order and average orientation angle of the molecules in the film. A series of experiments on hexadecane-stearic acid films supported the hypothesis that boundary films are highly ordered.

These results are very encouraging in that they demonstrate the possibility of long-range order even at low or zero loadings. At the extremely high loadings encountered in boundary lubricated systems it is expected that the degree of order would be even higher. Unfortunately, because of the relative fragility of germanium and other IR-transmitting materials, it is not possible to use the ATR technique to study films at high pressures; other techniques must be utilized.

After some background investigation, workers at Battelle decided to develop further the diamond anvil cell as a tool for the study of lubricants under high pressure. In this cell the material to be studied is placed between two opposed diamond faces mounted in separate pistons, one of which is movable. Force is transmitted to the diamond faces by means of a spring,

---

(1) Allen, C. M., Drauglis, E., Glaeser, W. A., Alexander, C. A., and Jakobsen, R. J., "Aircraft Propulsion Lubricating Film Additives: Boundary Surface Films" Report to Air Force Aero Propulsion Laboratory AFAPL-TR-73-121, Volume III, ADA029267, June, 1976.

(2) Allen, C. M. and Drauglis, E., "Boundary Lubrication: Monolayer or Multilayer", Wear, 14, 363 (1969).

screw and lever arm arrangement. For liquid specimens a gasket 1 to 5 mils thick is used to contain the material. The diameter of a specimen is on the order of 0.5 mm. This type of cell has been used to study pressure effects visually by means of optical microscopy (polarized and unpolarized) and by infrared spectroscopy.[3] In the past the usefulness of the apparatus has been severely limited because the low throughput of IR beams made it difficult to obtain good quality spectra. In the work performed at Battelle, this disadvantage was overcome by the use of a Fourier Transform infrared system and associated digital computer. Preliminary experiments performed on a polyphenyl ether and a solution of stearic acid in hexadecane produced results that indicated that the technique is capable of providing useful information on the properties of boundary lubricants at pressures as high as 100 kilobars.

Because of Battelle's success in these preliminary experiments, the diamond anvil cell technique was adopted as the principal experimental tool for the present program. It was expected that the information obtained on the high-pressure behavior of straight-chain hydrocarbons, fatty acids and solution of fatty acids in straight-chain hydrocarbons, along with studies of a typical diester lubricant, could be correlated with the results of the previous Aero Propulsion Laboratory program at Battelle. This should eventually lead to a more rational and systematic basis for the formulation of improved lubricants for use at the extreme conditions encountered by modern aerospace systems.

---

(3) Ferraro, J. R., "High Pressure Vibrational Spectroscopy" in Spectroscopy in Inorganic Chemistry, Vol. II, p. 57, C.N.R. Rao and J. R. Ferraro, eds., Academic Press, New York, 1971.

SECTION II

EXPERIMENTAL TECHNIQUE

Apparatus

The Diamond Anvil Cell

In recent years workers at Battelle and other laboratories have made considerable progress in high-pressure spectroscopic measurements in various modifications of the so-called diamond anvil cell[4-8]. This cell, originally developed by Weir, Lippincott, and Van Valkenberg[7] is perhaps the most useful cell yet invented for optical studies at high pressure.

The essential features of a tyical diamond anvil cell are given in Figure 1. The diamond anvils serve as the pressure transmitting elements as well as windows. These anvils are made of Type II diamonds, which are transparent in the ultraviolet, visible and infrared regions, except for the range 4 to 5.5 microns, where major absorption occurs. In practice, pressures of 100 kbar can be reached routinely. Still higher pressures up to 300 kbar may be reached but at great risk to the life of the diamonds. If liquids are to be studied, a metal gasket some 1 to 5 mils thick is commonly employed to contain the liquid between the diamond anvils.

Specimens contained within a diamond cell may be studied by means of X-rays, Raman spectroscopy, infrared spectroscopy, and optical microscopy. In some cases simple optical microscopy is sufficient to follow phase changes by observation of color changes and the sharp, easily discernible lines of demarcation between phases. Crossed polarizers can be employed to make the phase changes more visible. However, for some solids and for all organic liquids, optical microscopy is not sufficient to follow all of the changes that can occur; other means of observation must be employed. In the work at Battelle, infrared spectroscopy has been developed for studying organic

---

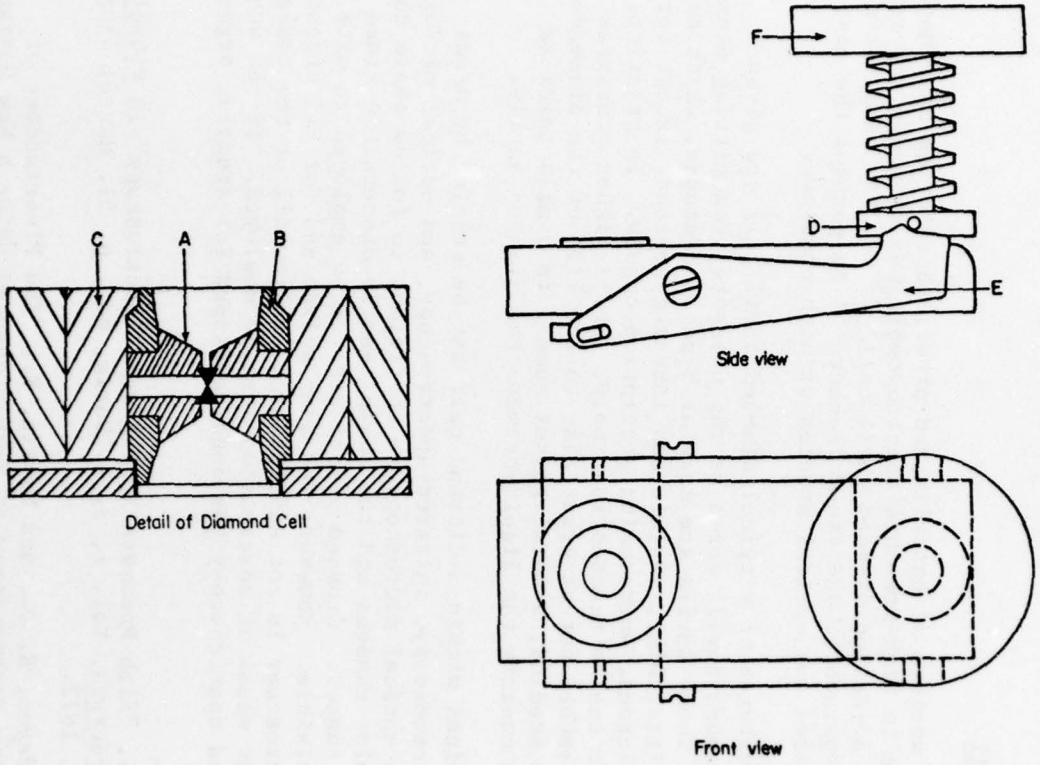
(4) Melveger, A. J., "High Pressure Vibrational Spectroscopy" in Vibrational Spectra and Structure, Vol. 1, J. R. Durig, ed., p. 51, Marcel Dekker, Inc., New York, 1972.

(5) Adams, D. M., Payne, S. J., and Martin, K., "The Fluorescence of Diamond and Raman Spectroscopy at High Pressures Using a New Design of Diamond Anvil Cell", Applied Spectroscopy, 27, 377 (1973).

(6) Lauer, J. L., "High Pressure Infrared Interferometry" in Fourier Transform Infrared Spectroscopy, J. R. Ferraro and L. J. Basil, eds. p. 169, Academic Press, New York, 1978.

(7) Ferraro, J. R. and Basile, L. J., "Spectroscopy at High Pressures--Status Report and Update of Instrumental Techniques", Applied Spectroscopy, 28, 505 (1974).

(8) Adams, D. M., and Payne, S. J., "Vibrational Spectroscopy of Solids at High Pressures", Annual Reports on Progress of Chemistry, 69A, 3 (1972).



A and B - Parts of Piston
C - Hardened Steel Insert
D - Presser Plate
E - Lever
F - Screw

Figure 1. Diamond Anvil High-Pressue Cell

materials in a diamond cell. The advantages of infrared are that it can give information about phase changes as well as changes in structure.

In the diamond anvil cell used at Battelle, the flat parts of the diamonds are only about 2 mm in diameter. When a metal gasket is used, the total area of the aperture is only on the order of 0.25 to 0.5 square mm. Because of this small aperture, a means of condensing the source infrared beams must be used. In the present work a 4X beam condenser designed and constructed by the Harrick Scientific Corporation was used.

Fourier Transform Infrared Spectroscopy

Even with an efficient beam condenser the amount of radiation passing through the aperture of a diamond anvil cell is so small that it is almost impossible to obtain satisfactory spectra with a conventional grating spectrometer. Fourier Transform Spectroscopy must be used. This type of spectroscopy differs from conventional dispersive infrared instruments in that the conventional spectrometer uses a monochromator to generate the spectral information whereas an interferometer is used for this purpose in FT-IR.[9] The use of an interferometer to obtain spectral information in the form of an interferogram (light intensity versus retardation) gives rise to a second difference between the two types of infrared spectroscopy, in that FT-IR systems use a dedicated computer to obtain the Fourier transform of the interferograms, converting them to the conventional infrared spectrum (light intensity versus wavelength or frequency). These two differences lead to the following major advantages of FT-IR over conventional IR systems:

(1) Substantial gain in energy of light throughput as compared to a monochromator. This gain in energy leads to a tenfold gain in sensitivity.[9]

(2) The ability to obtain complete spectra in a matter of seconds, enabling IR to be used in kinetic studies.

(3) Major data-handling advantages. The dedicated computer used with Fourier Transform systems allows storage of both interferograms and spectra, which may then be arithmetically manipulated. (For example, spectra may be ratioed against each other, subtracted, or smoothed.)

If not for the gain in sensitivity available by use of FT-IR, most of the spectra in this project could not have been obtained. Moreover, the use of the dedicated computer to analyze the spectra resulted in great savings in time and effort in obtaining the desired information about phase changes.

---

(9) Griffiths, P., Chemical Infrared Fourier Transform Spectroscopy, John Wiley & Sons, New York, 1975.

Procedures

Sample Preparation

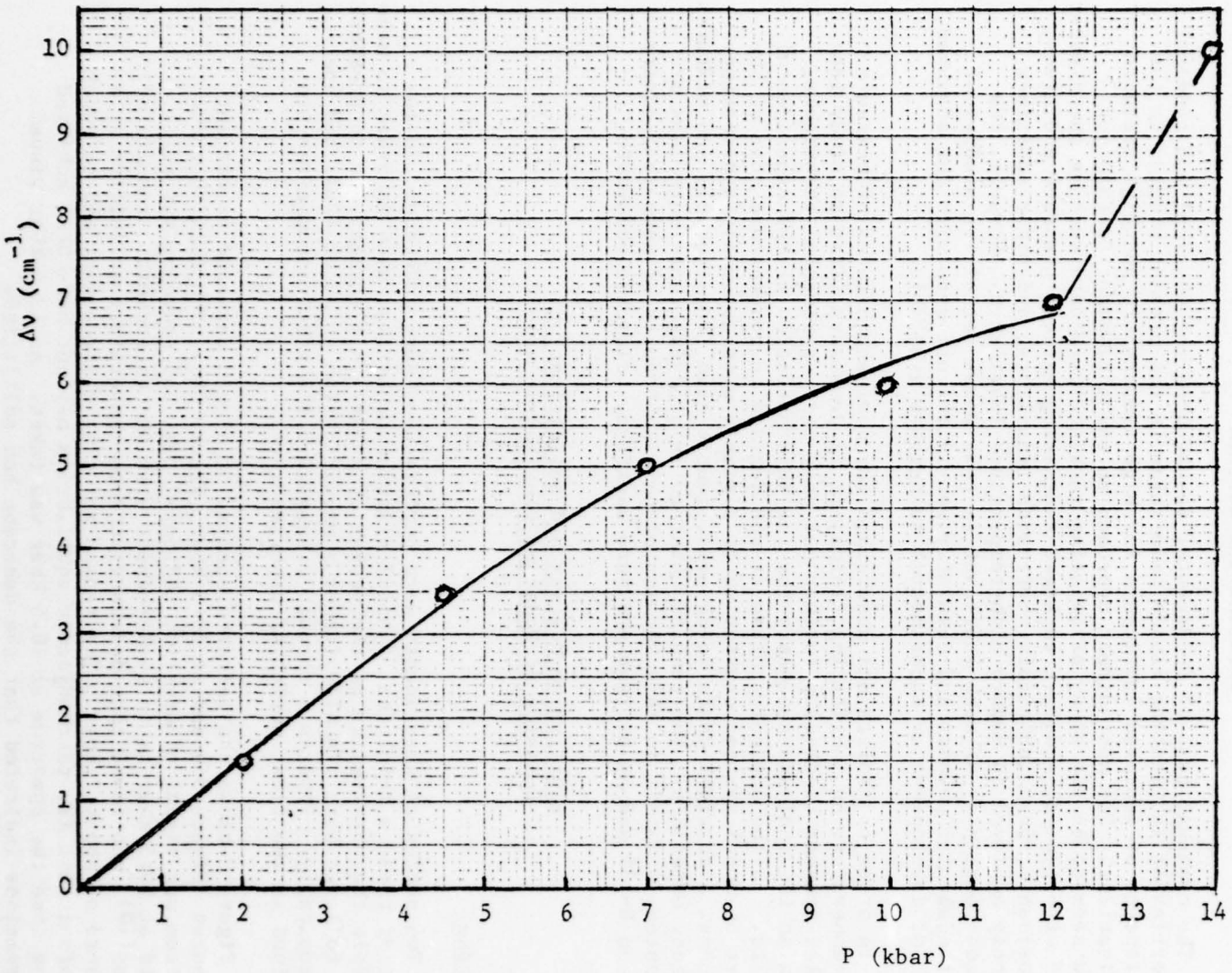
Both the samples of lauric acid and of dodecane were purchased commercially. Infrared spectra of these two samples did not give any evidence of impurities so the samples were used without further purification. The diester E-105 and the tricresyl phosphate (TCP) were obtained from the Aero Propulsion Laboratory and were used without further purification.

Stock solutions (by weight) of lauric acid in dodecane and of TCP in E-105 were prepared and stored. These stock solutions were used for the diamond cell solution experiments reported in the following sections.

Pressure Calibration

Because of the small sample volume of a diamond anvil cell, it is not possible to determine pressure within the cell by use of pressure transducers. Perhaps the simplest alternative method is the measurement of geometrical parameters, such as lever arm advantage and diamond face areas (within the gasket, of course) and a calibration of the spring constant. However, this method has been shown to be inaccurate because the spring compression--usually expressed in terms of the number of the compressing screw turns--depends too much on gasket flow and hysteresis to be a reproducible pressure parameter[6].

A far superior method of calibrating the cell has been developed by J. W. Brasch of the Naval Surface Weapons Center. This method is based on measuring the frequency shift of the 660 cm^{-1} band of nitromethane. Mr. Brasch supplied us with pressure versus frequency data which he obtained by placing a very small ruby chip in a sample of nitromethane in a diamond anvil cell. The frequency shift of the ruby line has already been related to pressure by a group at the National Bureau of Standards headed by G. J. Piermarini. Then, determining the ruby frequency shifts and the 660 cm^{-1} nitromethane frequency shifts, gives us a means of accurately determining pressures by relating the nitromethane frequency shifts to number of turns of the screw. The pressure calibration curve for the 660 cm^{-1} nitromethane line is given in Figure 2.



($\Delta\nu$ for the 660 cm^{-1} band of CH_3NO_2 versus pressure)

Figure 2. Pressure Calibration Curve

SECTION III

EXPERIMENTAL RESULTS

The eventual goal of fundamental research on the physical and chemical properties of lubricating fluids undertaken in the present program is the development of improved lubricants for high temperature and high pressure applications. The most direct approach to the attainment of this goal would seem to be the study of existing turbine lubricants such as the diester E-105 with typical additive packages containing extreme pressure additives, antioxidants, foam inhibitors, corrosion inhibitors, and other additives commonly employed in modern high-temperature lubricants. However, the extreme complexity of such lubricant systems makes definitive studies of the fundamental physics and chemistry very difficult even with the advanced state of development of experimental techniques available.

In order to isolate and understand the dominant effects of pressure and temperature on lubricating fluids, it is necessary first to study less complex systems to develop further not only the experimental techniques, but also the analysis necessary for the interpretation of the experimental results. In the present program it was decided to concentrate most of the effort on model systems consisting of a simple straight-chain hydrocarbon, dodecane, a straight-chain fatty acid, lauric acid (dodecanoic), and mixtures of these materials. The results obtained in studying these materials are presented in detail in this section along with results of some preliminary work on E-105 and an extreme pressure additive, tricresyl phosphate.

Equilibrium Melting and Solidification Behavior of Dodecane Plus Lauric Acid

Dodecane

Two series of experiments were performed on pure dodecane. In the first of these a thick (ca. 5 mils) platinum gasket was used in order to make possible the observation of the weaker IR bands. All changes due to pressure were followed both visually (under a magnification of about 100X) and spectroscopically. Figures 3 through 7 summarize the spectroscopic results obtained in the first series of experiments.

Figure 3 shows the infrared spectra of liquid dodecane at ambient pressures (Figure 3A) and at 10.5 kbar (Figure 3B). The fact that the spectrum and visual observation indicated that the dodecane was still liquid at 10.5 kbar is in disagreement with the dilatometric results of Nelson[10], who found that dodecane at room temperature solidifies at a pressure of about 2 kbar. The reason for this disagreement may be superpression; that is, thermodynamic equilibrium may not have been achieved at the time the spectrum at 10.5 kbar was taken. At 13.5 kbar visual observations indicated that the dodecane had solidified.

---

(10) Snyder, R. G., "Vibrational Study of the Chemical Conformation of the Liquid n-Paraffins and Molten Polyethylene", J. Chem. Phys., 47, 1316 (1967).

Comparison of the spectra of Figures 3A and 3B indicates that there is little change in liquid dodecane with increasing pressure. This is further illustrated in Figure 4A which shows the results of subtracting the spectrum of Figure 3A from that of Figure 3B. From this difference spectrum it can be seen that the only effects of increasing pressure on liquid dodecane are a slight increase in the CH_2 bending frequency near 1455 cm^{-1} and an increase in the intensity of the CH_2 rock-twist frequency near 715 cm^{-1}. However, comparison of the spectra of Figures 3B and 3C indicates that solidification brings about more pronounced changes. These changes are illustrated in Figure 4B which shows the results of subtracting the spectrum of Figure 1C from that of Figure 3B. Many different changes in intensity in bands such as the 1112 cm^{-1} C-C stretch and the 895 cm^{-1} CH_3 rock are observed as well as shifts in frequency in bands such as the 1455 cm^{-1} band and the 715 cm^{-1} band.

Figure 5 illustrates the effects of pressure on the spectra of solid dodecane. The difference spectrum of Figure 4B is repeated in Figure 5A in order to facilitate comparison with difference spectra obtained on solid dodecane at higher pressures given in Figure 5B and Figure 5C. Figure 5B greatly resembles Figure 5A. That is, Figure 5B shows the same changes as were observed when solidifying liquid dodecane. Figure 5C, which shows the difference spectrum for solid dodecane at higher pressures than those in Figure 5B, is more typical of the effects of pressure on the spectra of solids than Figure 5B. These effects are increasing intensities and frequencies with increasing pressure. The probable reason for the anomaly in Figure 5B is that the specimen was only partially solidified at 13.5 kbar because thermodynamic equilibrium has not yet been attained when the spectrum was taken.

With proper care, single crystals can be grown in the diamond cell. Polarized spectra obtained on a single crystal of dodecane are given in Figure 6. These spectra exhibit a rather high dichroic ratio indicating that the axis of polarization must have been very close to the crystal axis. After the spectra in Figure 6 were obtained, the specimen was melted (by decreasing the pressure) and a polycrystalline mass was obtained by rapidly increasing the pressure again. Polarized spectra were then obtained (Figure 7). Somwhat smaller dichroic ratios were obtained.

After the conclusion of the studies of dodecane with a thick gasket, a thin (1 mil) gasket was prepared and the cell reloaded with dodecane. The pressure was increased to 10 kbar after obtaining a spectrum at ambient pressure. This spectrum showed that the dodecane was still liquid. However, when the cell was placed under the microscope in preparation for futher pressure increases, it was observed that the specimen had partially crystallized. Since the crystal appeared to be growing with time, spectra were taken every few hours until it appeared that the liquid had completely crystallized, a process which took about 12 hours. A spectrum of the resulting solid was taken and the pressure was then increased to 14 kbar, at which pressure a phase change of some kind may have occurred. Spectra were taken at this pressure and then at 24 kbar.

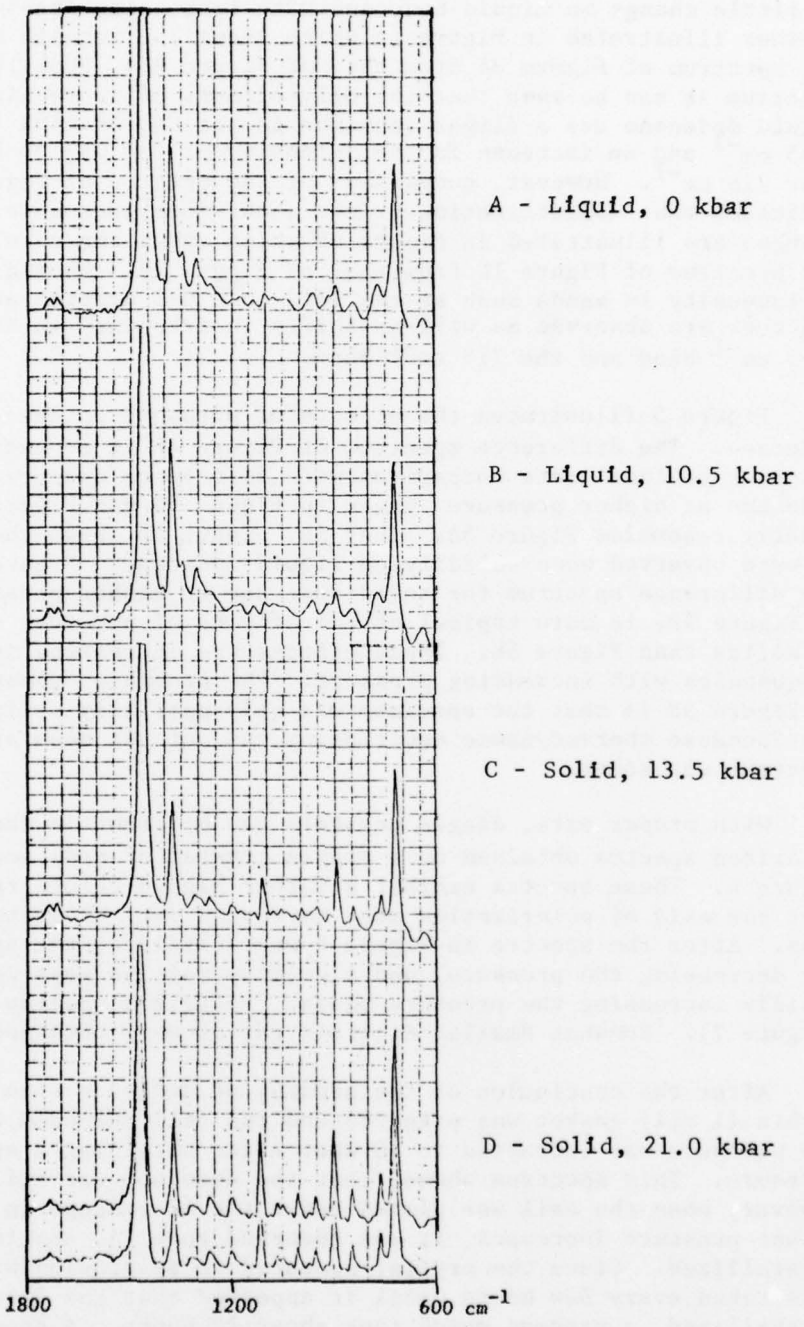
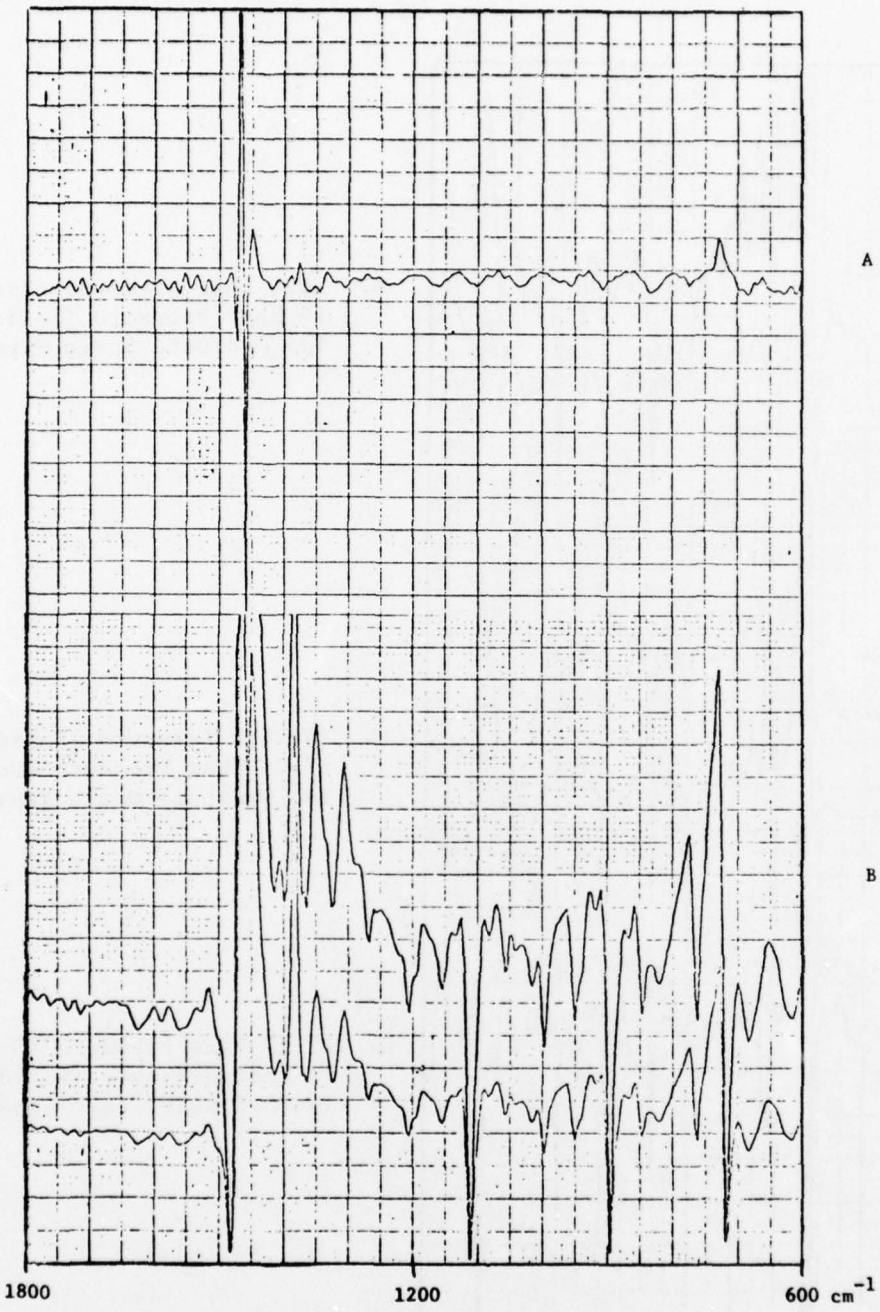
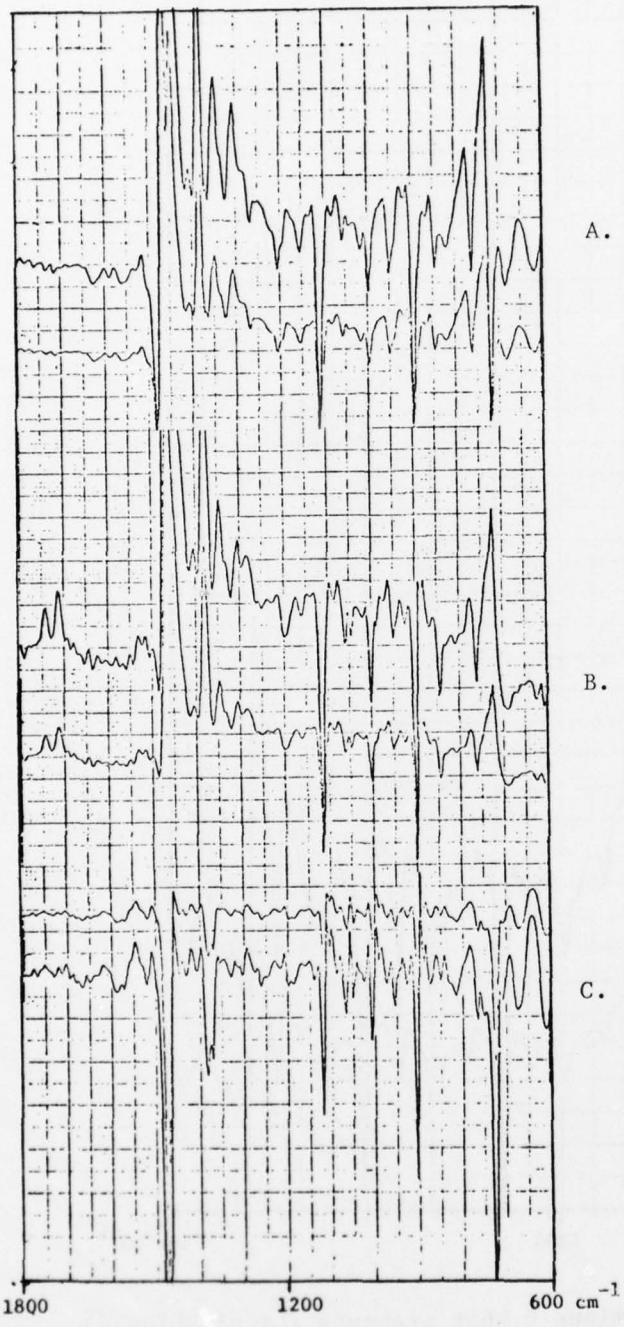


Figure 3. Infrared Spectra of Dodecane at Various Pressures



A = 10.5 kbar pressure minus 0 kbar pressure (Liquid-Liquid)
B = 10.5 kbar pressure minus 13.5 kbar pressure (Liquid-Solid)

Figure 4. Subtracted Infrared Spectra of Dodecane at Various Pressures



A. 10.5 kbar Pressure (Liquid) minus 14 kbar Pressure (Solid) at Two Ordinate Scale Expansions

B. 14 kbar Pressure (Solid) minus 17.25 kbar Pressure (Solid) at Two Ordinate Scale Expansions

C. 17.25 kbar Pressure (Solid) minus 21 kbar Pressure (Solid) at Two Ordinate Scale Expansions

Figure 5. Subtracted Infrared Spectra of Dodecane at Various Pressures

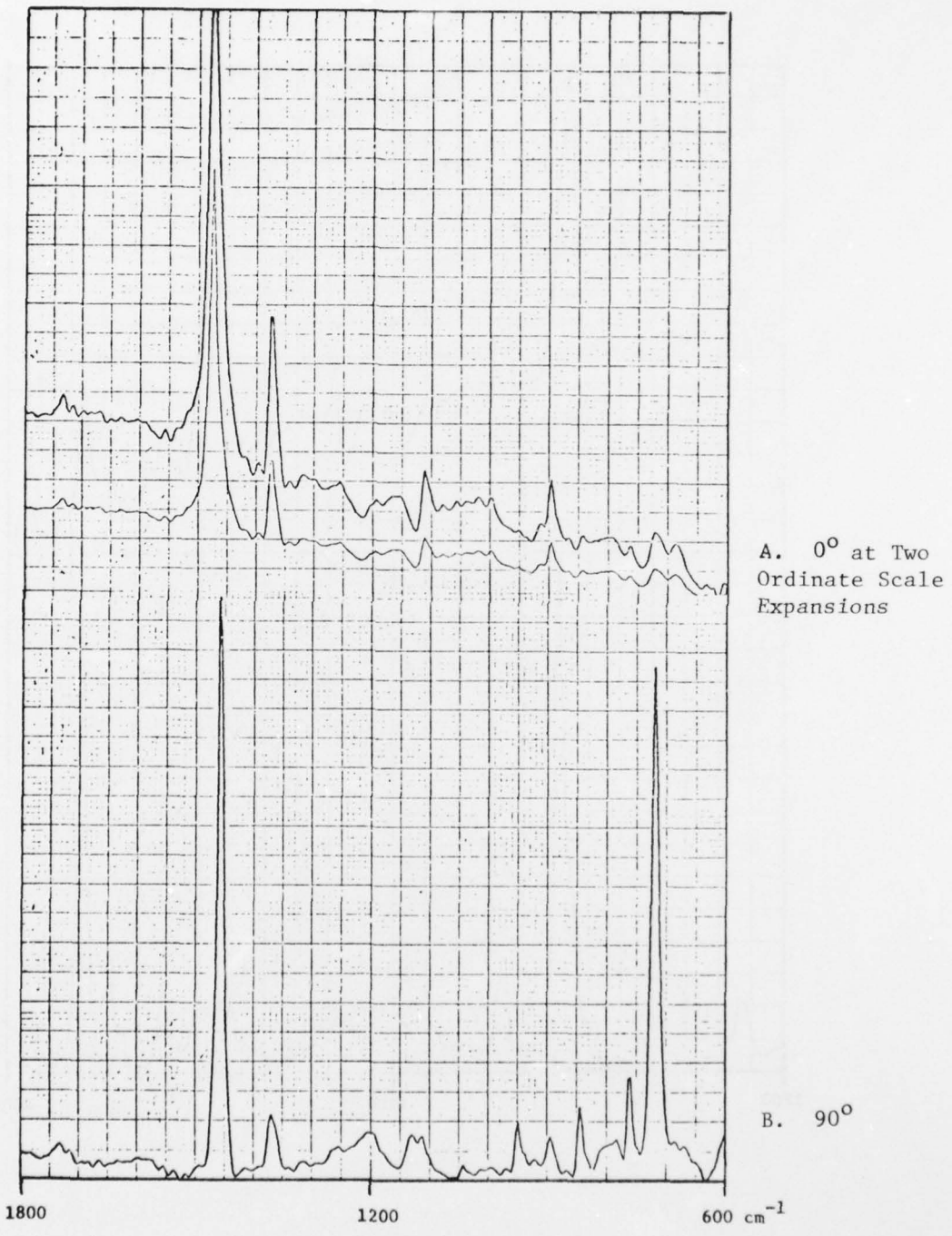


Figure 6. Polarized Infrared Spectra of Single Crystal Dodecane at 16.5 kbar Pressure

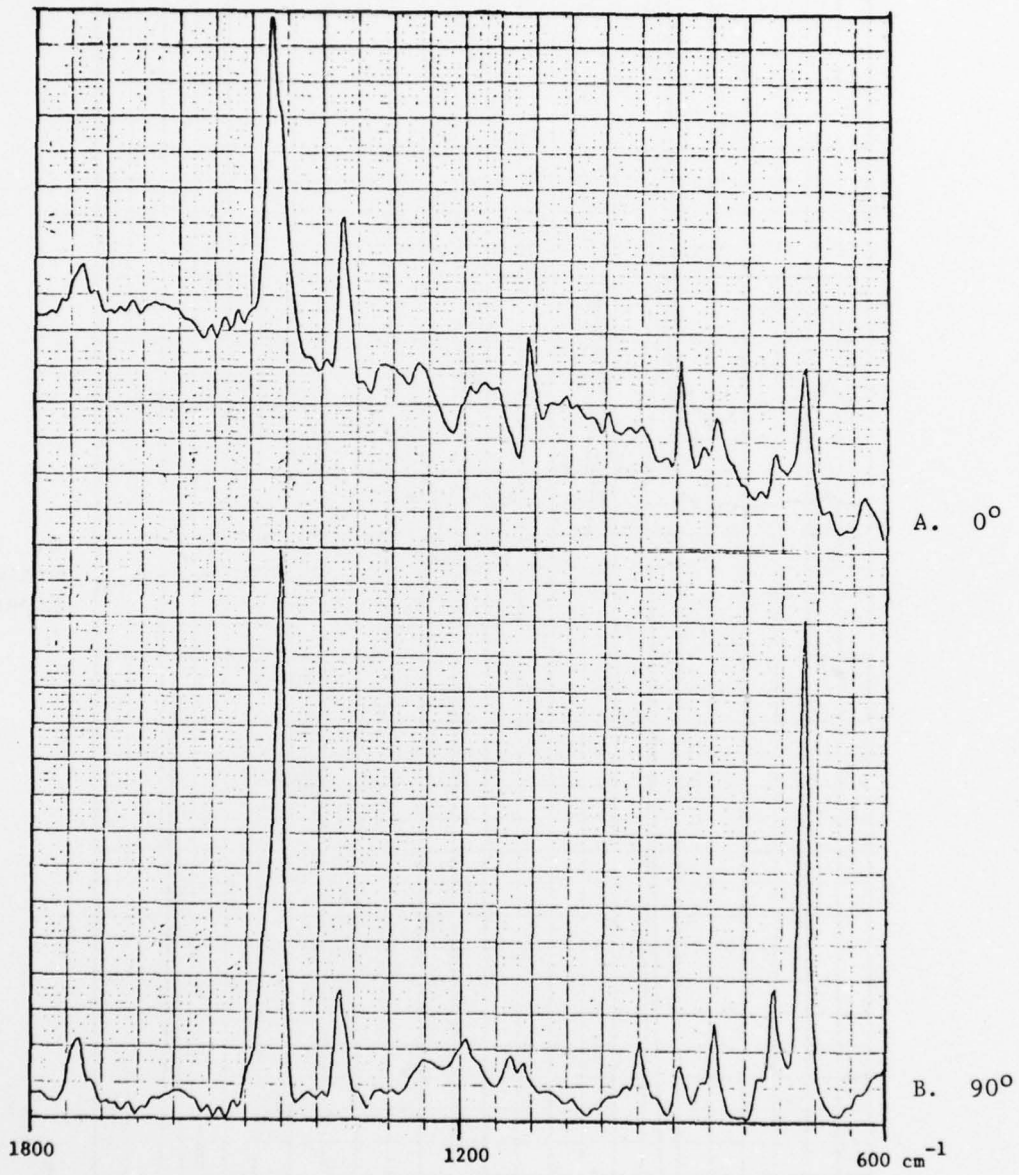


Figure 7. Polarized Infrared Spectra of Polycrystalline Dodecane at 16.5 kbar Pressure

Various difference spectra are shown in Figure 8. Figure 8A shows the subtraction of the liquid spectrum at ambient pressure and the spectrum at 10 kbar. The subtracted spectrum of Figure 8A is identical to the results to be expected from the subtraction of liquid dodecane at two different pressures (a slight increase in the intensity of the CH_2 bending frequency near 1455 cm^{-1} and the rock-twist frequency near 715 cm^{-1}).

The difference spectrum between the initial spectrum obtained at 10 kbar and the spectrum obtained after 1 hours at 10 kbar is given in Figure 10B. These changes are similar to the differences between liquid and solid dodecane with the exception that the bands which appear on solidification are weaker in comparison with the bands which disappear or lose intensity on solidification. (The bands which appear on solidification are 112, 895, and 715 cm^{-1}, while the bands which lose intensity are near 1455 and 1382 cm^{-1}.) These difference spectra demonstrate that at 10 kbar pressure, the dodecane was slowly becoming more crystalline. Figure 8C shows the difference spectrum between 1 hour at 10 kbar and 21 hours at 10 kbar pressure. This is very similar to Figure 8B and indicates that the dodecane is still solidifying at 10 kbar.

The difference spectrum between the overnight 10 kbar spectrum and the spectrum at 14 kbar is shown in Figure 8D. Again, the spectral changes are similar to those observed in Figures 8B and 8C. This demonstrates that even after standing overnight and even though the sample appeared to be visually entirely crystalline, that the changes which occurred at 14 kbar were further solidification of the dodecane. The difference between 14 and 24 kbar pressure is shown in Figure 8E. Here all the infrared bands are gaining intensity with increasing pressure which indicates that the sample was completely crystallized at 14 kbar.

The pressure was then lowered to 10 kbar and a spectrum was obtained. The difference spectrum between the 24 kbar spectrum and the 10 kbar reverse spectrum is given in Figure 9A. Virtually no changes are observed indicating that the sample is still completely crystalline at a pressure of 10 kbar. The pressure was then lowered to 2 kbar and then to less than 1 kbar with spectra obtained at each pressure. A slight decrease in pressure then melted the dodecane. The subtraction between the 10 kbar reverse spectrum and the 2 kbar reverse spectrum is shown in Figure 9B, while the subtraction between the 2 kbar reverse spectrum and the 1 kbar reverse spectrum is shown in Figure 9C. In each case the loss of bands at 1112 and 895 cm^{-1} indicates that the dodecane is losing crystallinity as the pressure is released. However, the microscopic observations at these pressures do not show any evidence of melting.

Lauric Acid

Pure lauric acid (a solid at room temperature) was loaded in the diamond cell by filling the platinum gasket hole with solid lauric acid and then warming the cell until melting of the acid. The cell was then placed in the FT-IR instrument and spectra were obtained. Loading the cell by the

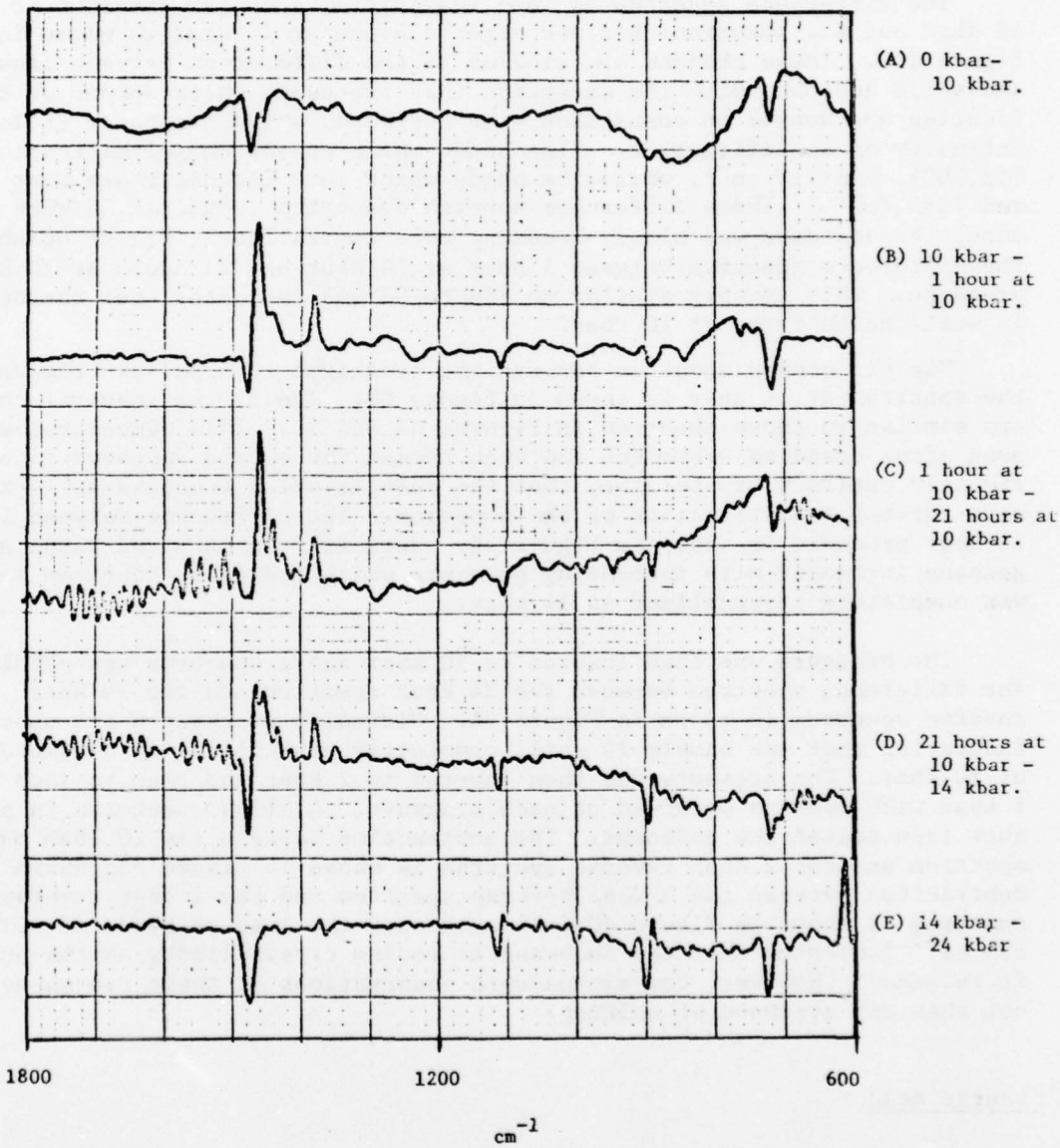
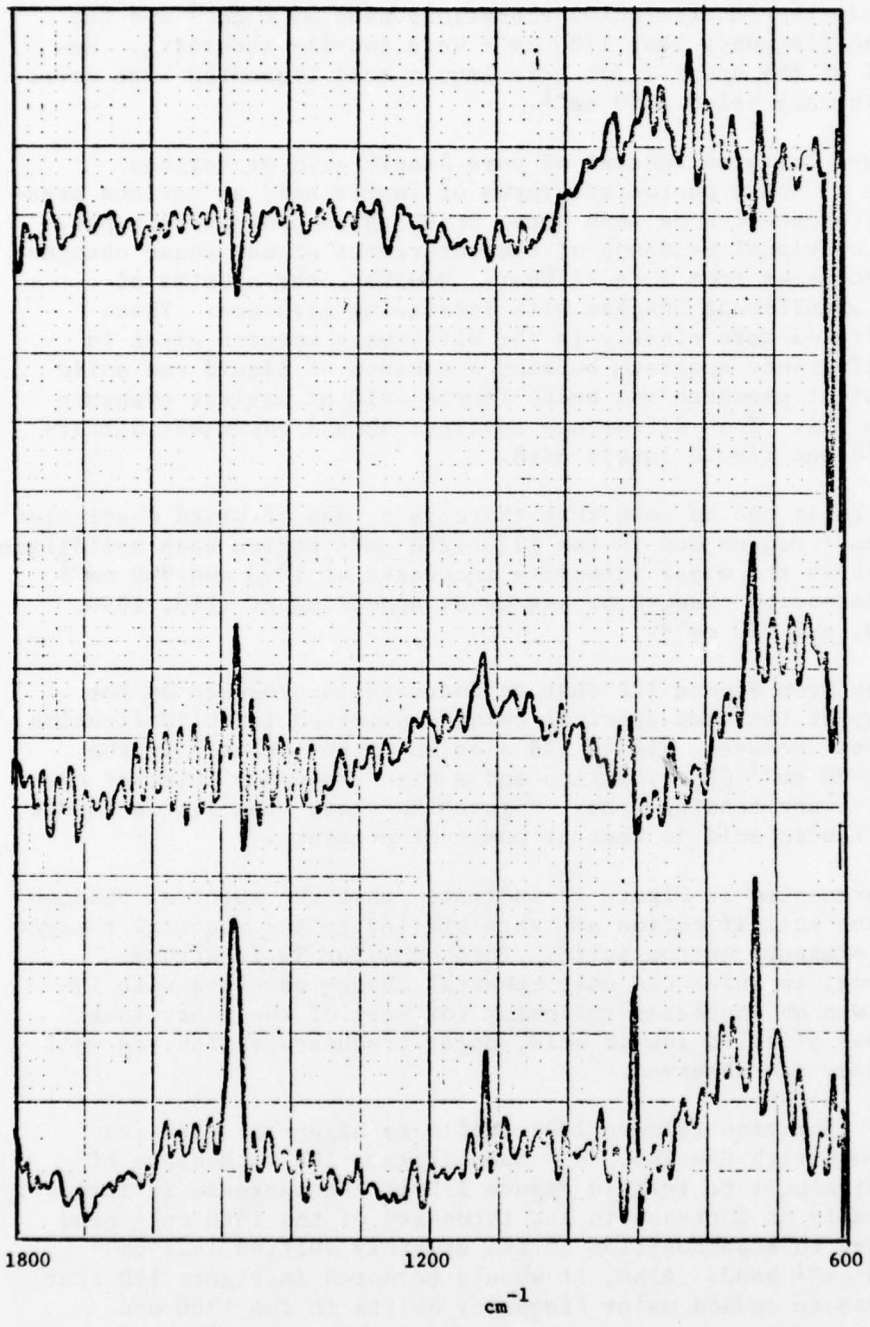


Figure 8. Subtracted Infrared Spectra of Dodecane at Various Pressures (Increasing)



(A) 24 kbar minus 10 kbar-reverse

(B) 10 kbar reverse, minus 2 kbar-reverse

(C) 2 kbar reverse, minus <1 kbar-reverse

Figure 9. Substracted Infrared Spectra of Dodecane at Various Pressures (Decreasing)

above-described technique resulted in a very thick sample and spectra, which were so intense that the CH stretching vibrations near 2900 cm^{-1} and the carbonyl stretching frequency near 1700 cm^{-1} were totally absorbing. Because of this, all of the spectra for pure lauric acid presented here cover the spectral region only below 1600 cm^{-1}.

Figure 10 shows infrared spectra of pure lauric acid at various pressures. Figure 11 shows photomicrographs of lauric acid at various pressures. Little difference can be seen among these three photomicrographs. That is, there is no visual evidence of the occurrence of any phase changes as the pressure increases from 4 to 24 kbar. However, the spectra of Figure 8 indicate significant changes with increasing pressure. These changes are illustrated more clearly in the difference spectra given in Figure 12. The difference spectrum between a mixture of liquid and solid lauric acid at ambient pressure and solid lauric acid at ambient pressure is given in Figure 12A. This difference spectrum should represent differences between solid and liquid lauric acid.

From Figure 12A it can be seen that there is a loss of broad absorption in the 1420-1460 cm^{-1} region and in the 1220-1280 cm^{-1} region upon solidification. Moreover, there are major intensity increases at 1300 and 940 cm^{-1} and either minor intensity changes or new bands appearing at 1195, 1090, 875, 785, 730, 690, and 550 cm^{-1}.

It can be seen from Figure 12B that an increase in pressure on the solid leads to many of the same spectral changes observed in solidification at ambient pressure. However, Figure 12B also shows an increase in the intensity of the 1460 cm^{-1} CH_2 vibration and a high frequency shift of the 940 cm^{-1} OH out-of-plane bending mode. Figure 12C shows that little change occurs when solid lauric acid is kept at constant pressure.

The results presented in Figure 12 indicate that the spectral changes for lauric acid upon solidification are very similar to the spectral changes due to increasing pressure on the solid. This behavior is in strong contrast to dodecane, in which the only spectral change observed with increasing pressure was an increased intensity for most of the vibrations. However, in the case of solid lauric acid, major frequency shifts, as well as intensity changes, are observed.

The 1425 cm^{-1} vibration (Figure 10D) shifts to higher frequencies and eventually blends with the 1460 cm^{-1} band (Figure 10E). Because of this shift it is difficult to tell in Figure 12D if the increase in intensity at 1460 cm^{-1} is really an increase in the intensity of the 1460 cm^{-1} band or whether it is due to superposition of the upwardly shifted 1425 cm^{-1} band with the 1460 cm^{-1} band. Also, it should be noted in Figure 12D that increasing the pressure causes major frequency shifts in the 1300 and 940 cm^{-1} bands.

The principal reason for the difference in spectral changes of dodecane and lauric acid is the existence of hydrogen bonding in lauric acid.

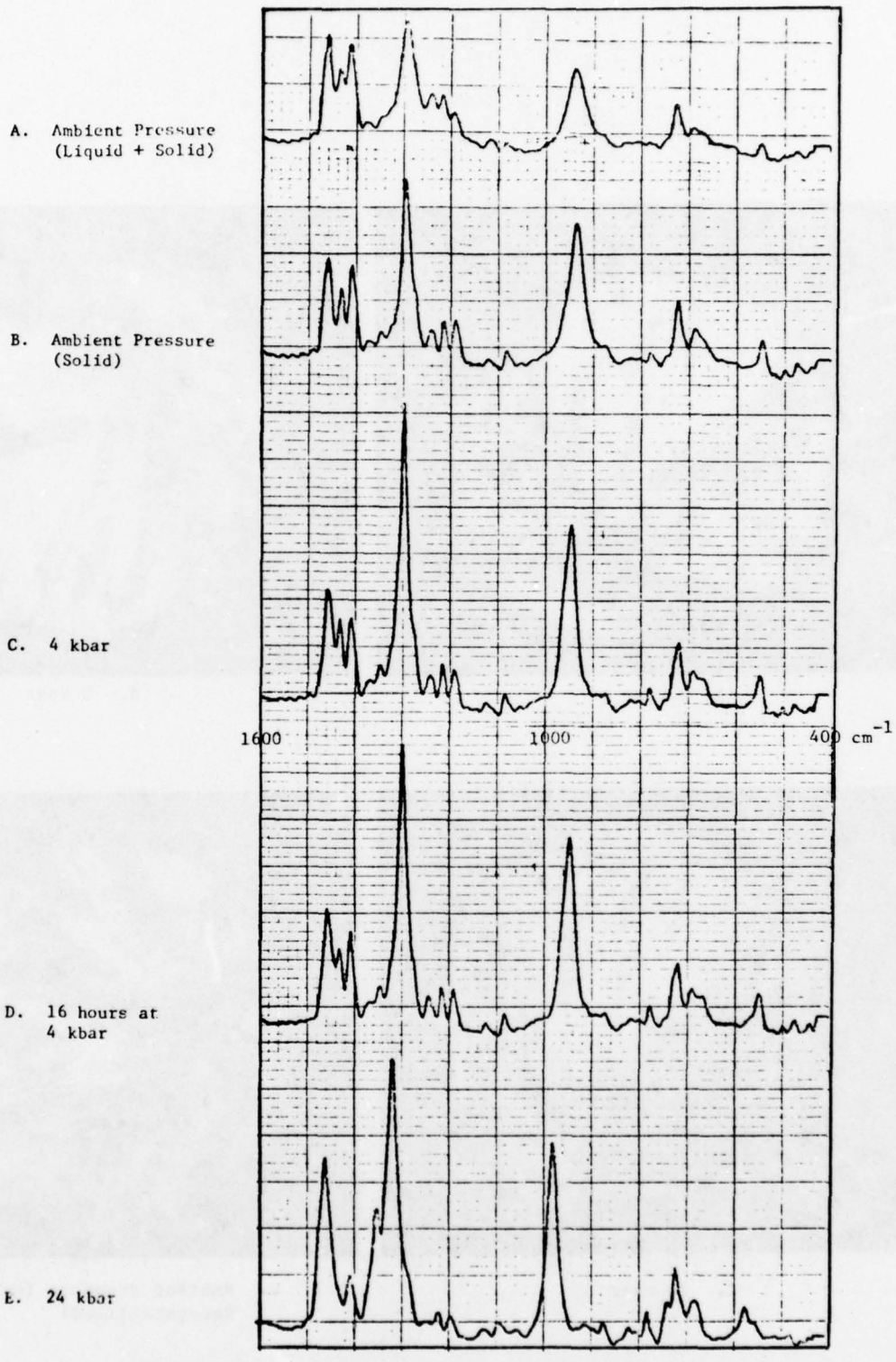
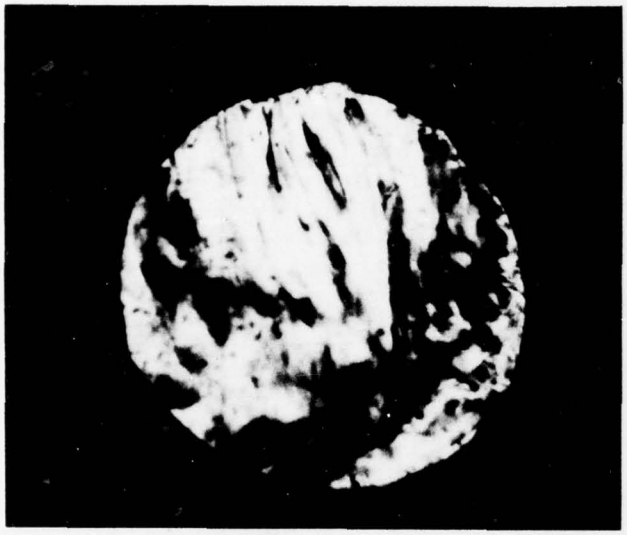
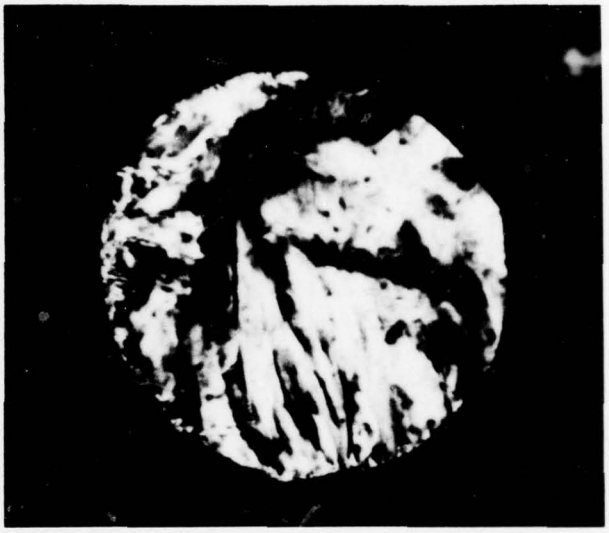


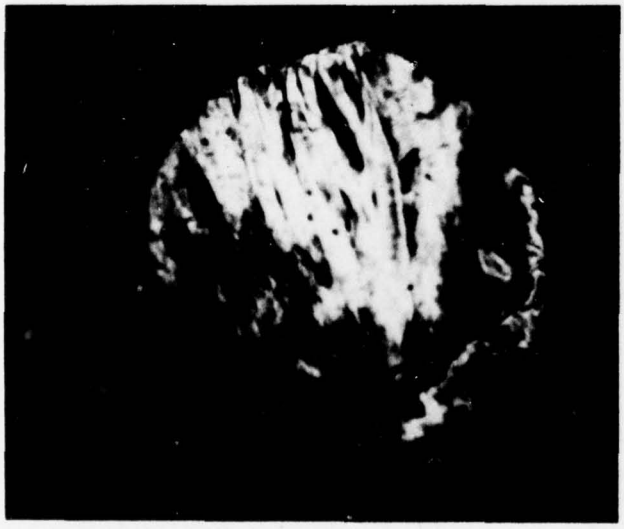
Figure 10. Infrared Spectra of Lauric Acid



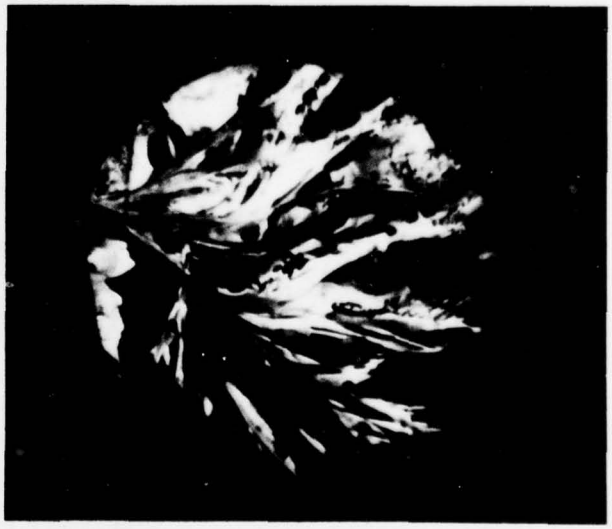
A. 4 kbar



B. 9 kbar



C. 24 kbar



D. Ambient Pressure (Melted and Recrystallized)

FIGURE 11. PHOTOMICROGRAPHS OF LAURIC ACIDS

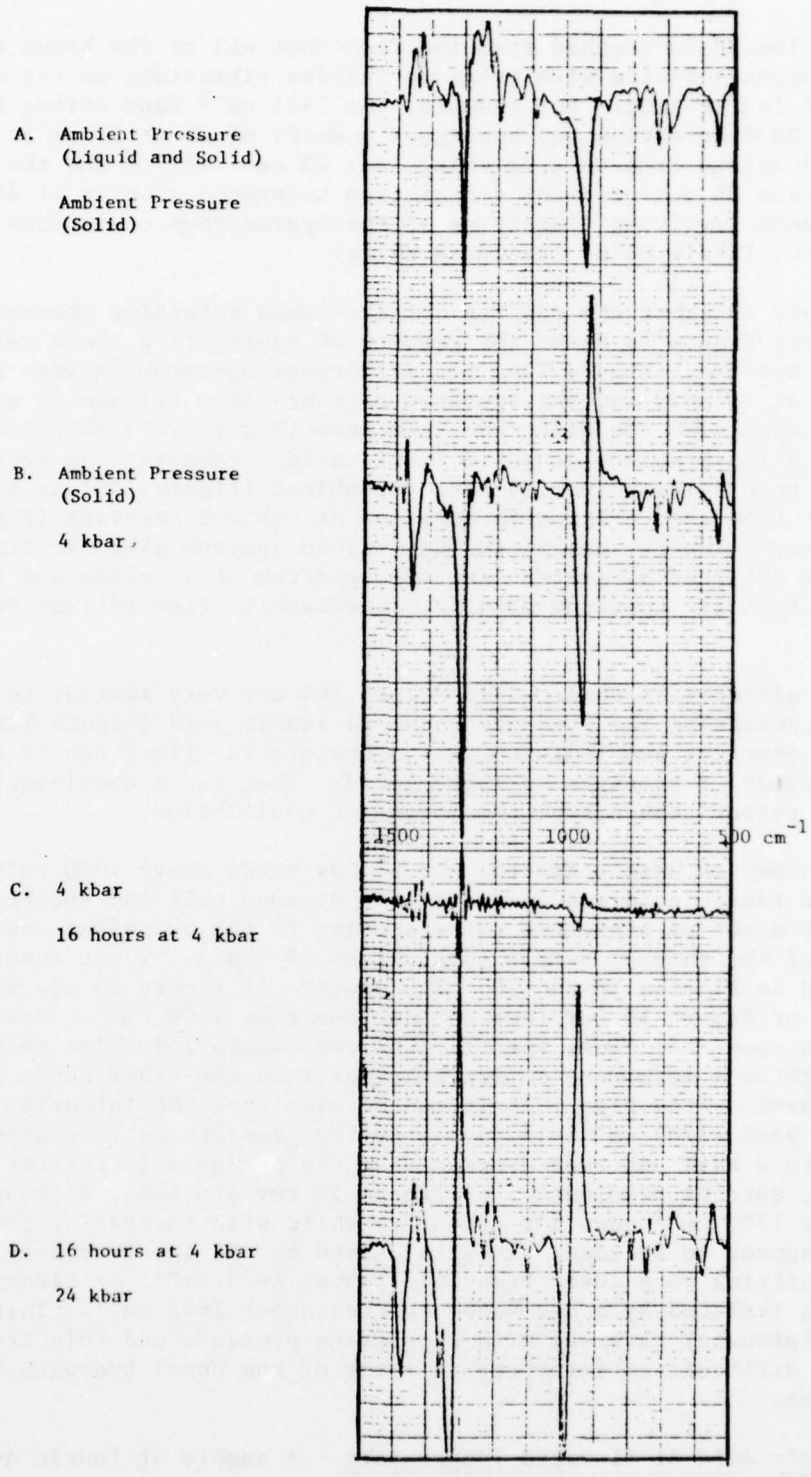


Figure 12. Subtracted Infrared Spectra of Lauric Acid

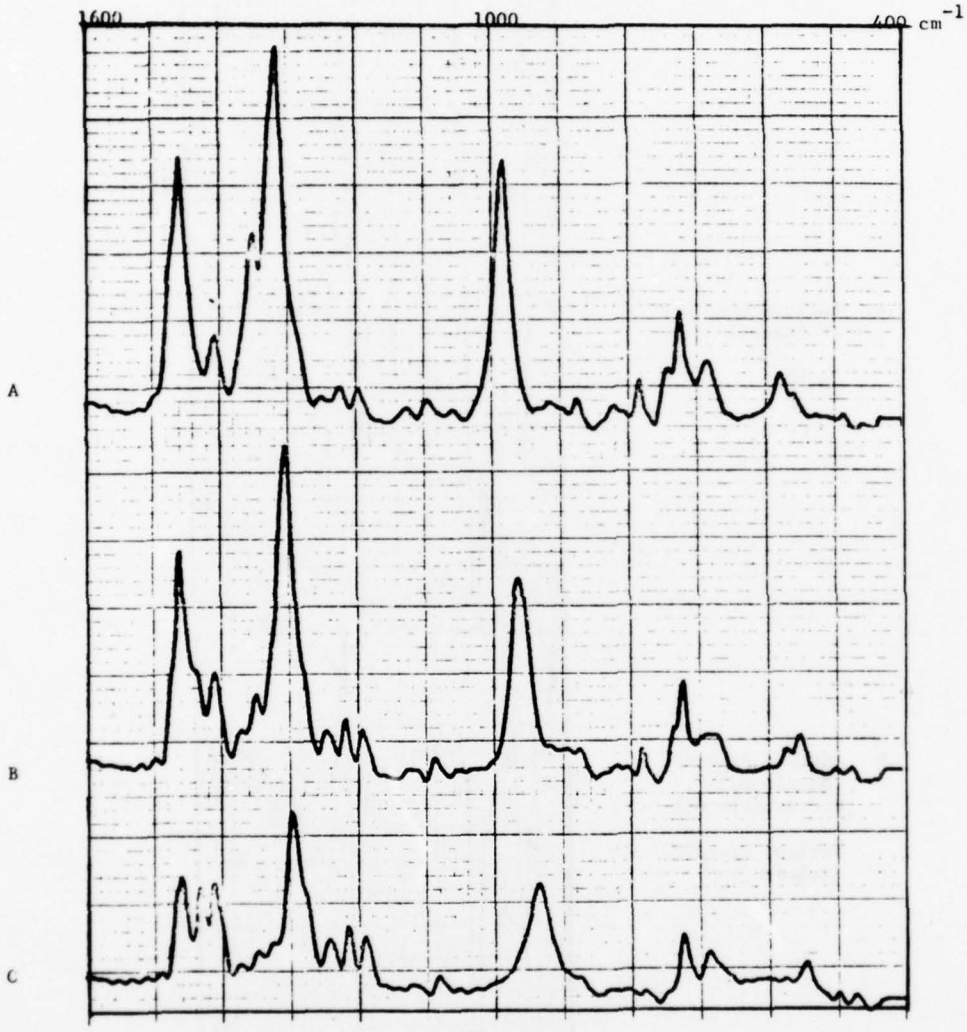
This conclusion is reached from the fact that all of the bands which showed large frequency shifts with pressure involve vibrations of the OH or CO groups of lauric acid. For example, the 1425 cm^{-1} band arises from the in-plane OH deformation and undergoes a shift of about 30 cm^{-1}; the 1300 cm^{-1} band arises from CO stretching (ca. 25 cm^{-1} shift) and the 940 cm^{-1} arising from OH out-of-plane deformation undergoes a shift of 40 to 50 cm^{-1}. The IR bands involving vibrations of the hydrocarbon chain show an intensity change, but little or no frequency shift.

Figure 13 shows the spectra obtained when releasing pressure on lauric acid, while Figure 14 shows the results of subtracting these releasing pressure spectra. Figure 14A, the difference spectrum between the spectrum obtained at 24 kbar and the spectrum obtained upon release to ambient pressure, is much like the difference spectrum (Figure 12D) obtained from increasing the pressure on solid lauric acid. However, the spectrum obtained upon release from 24 kbar to ambient (Figure 13B) is significantly different from that originally obtained at ambient pressure (Figure 10B). This is more clearly seen in the difference specrum given in Figure 14B, which was obtained by subtracting the spectrum of a melted and recrystallized specimen from the spectrum obtained immediately after release to ambient pressure.

The differences observed in Figure 14B are very similar to those seen in increasing the pressure on solid lauric acid (Figure 12B). These spectral observations indicate that a hysteresis effect can be obtained by rapid release of pressure on lauric acid. That is, a quasi-equilibrium is obtained rather than a true thermodynamic equilibrium.

In order to obtain spectra which show bands above 1600 cm^{-1}, a thinner sample of lauric acid was loaded in the diamond cell and spectra were taken for a set of pressures corresponding to the pressures used in the studies of the thicker sample (ambient to 24 kbar). These spectra are presented in Figures 15 and 16. The spectra of Figure 15 are very similar to those of Figure 10 for frequencies less than 1600 cm^{-1}. However, it can be seen from these spectra that the carbonyl doublet near 1700 cm^{-1} exhibits a much more comlex behavior than the other bands as pressure is increased. From Figure 16 it can be seen that the intensity of the carbonyl band (1705 cm^{-1}) increases as the pressure is increased from ambient to 4 kbar and then decreases as the pressure is further increased. Moreover, careful examination of Figure 15 reveals that, although the peak near 1705 cm^{-1} does not appear to shift with increasing pressure, it does appear to broaden. This is caused by the shoulder near 1690 cm^{-1} either shifting to a lower frequency (about 1675 cm^{-1}) or disappearing and being replaced by a new band centered about 1675 cm^{-1}. This combination of intensity reversal with increasing pressure and this frequency shift is difficult to interpret in terms of the usual hydrogen bonded structures.

Lauric Acid At Elevated Temperature. A sample of lauric acid was loaded in the diamond cell by filling the gasket with solid lauric acid



A - 24 kbar
B - Ambient Pressure (Released from 24 kbar)
C - Ambient Pressure (Melted and Recrystallized)

Figure 13. Infrared Spectra of Lauric Acid

A. Ambient Pressure
(Released)

24 kbar

B. Ambient Pressure
(Melted and
Recrystallized)

Ambient Pressure
(Released)

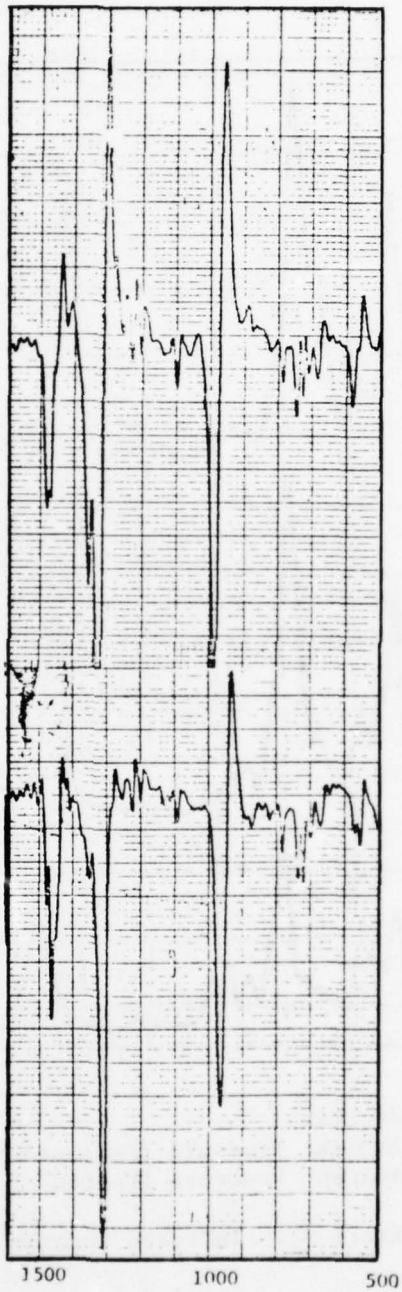


Figure 14. Subtracted Infrared Spectra of Lauric Acid

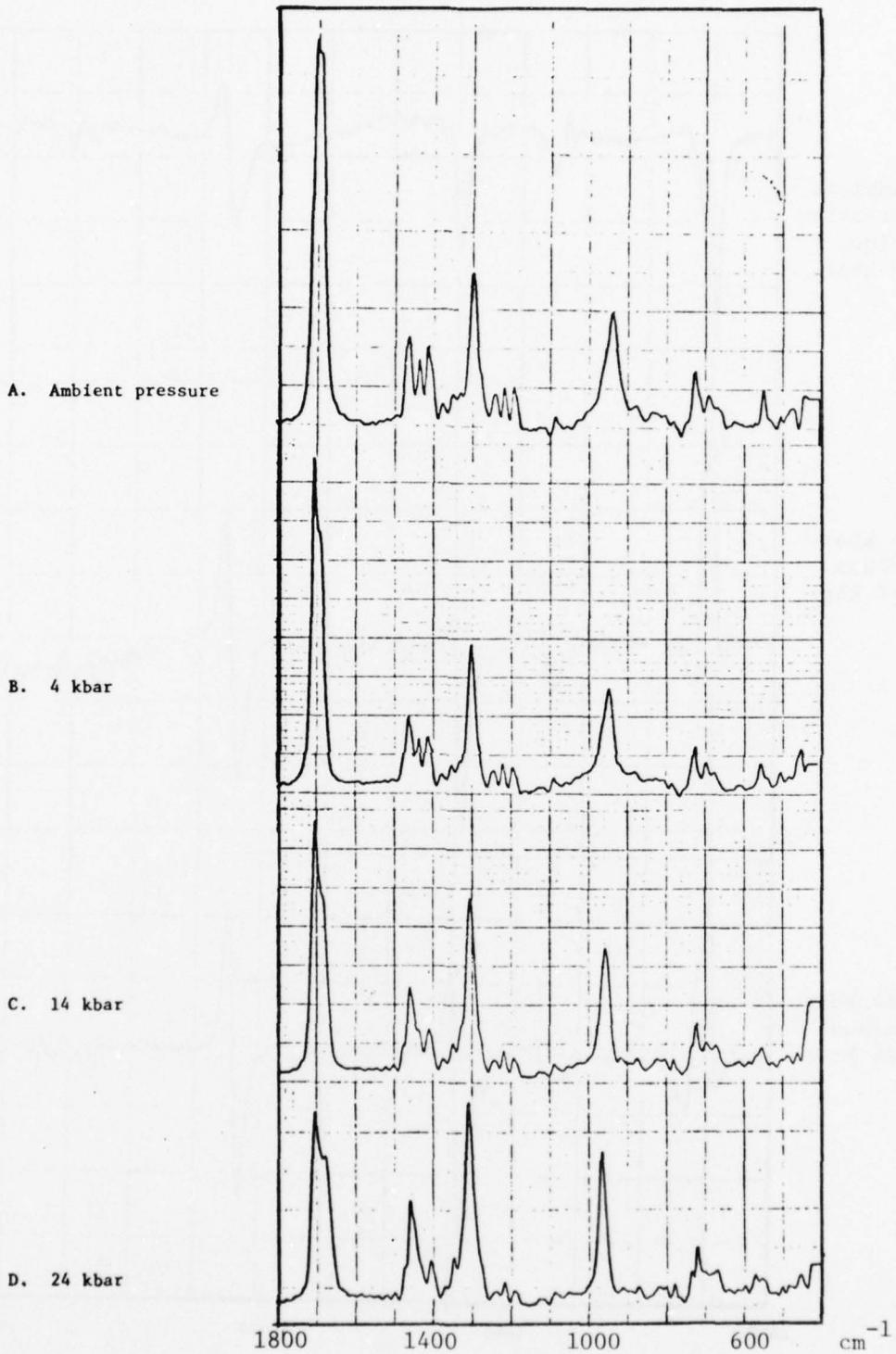


Figure 15. Infrared Spectra of Lauric Acid

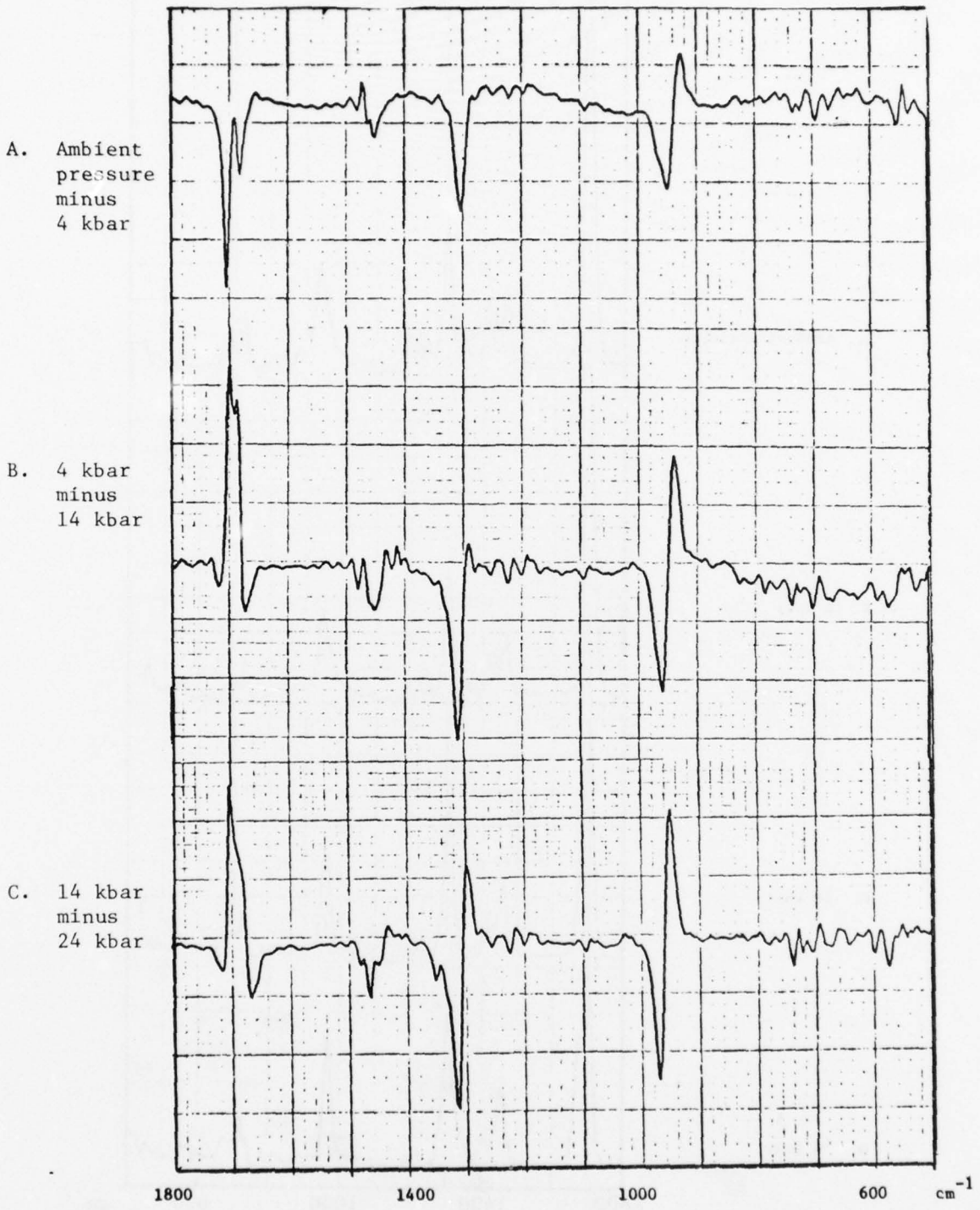


Figure 16. Subtracted Infrared Spectra of Lauric Acid

and then warming the cell until the acid melted. The cell was then allowed to cool to room temperature when the acid solidified. A slight pressure was applied to make certain that the cell was sealed and then the cell was heated to 100 C. During the heating process, the lauric acid melted. Spectra were then obtained at various pressures while at 100 C. Some of these spectra are shown in Figure 17 while Figure 18 shows the subtraction of various pairs of pressure spectra.

Figure 18A shows the result of subtracting the spectrum at 9 kbar, pressure from that at 4 kbar pressure. Microscopic and spectra (see Figure 17A) evidence indicate that the sample is still liquid at 9 kbar pressure. Figure 18A indicates that the only effect of raising the pressure on liquid lauric acid is a small shift of the carbonyl vibration (~1720 cm^{-1}) to lower frequencies. When the pressure was raised to 14 kbar, lauric acid remained a liquid and the result of subtracting the 14 kbar spectrum from the 9 kbar spectrum are shown in Figure 16B. In Figure 16B, the low frequency shift of the carbonyl frequency is more pronounced and there are small increases in intensity of the 1460 and the 1290 cm^{-1} vibrations.

At 100 C, microscopic observation indicated that lauric acid solidifies when the pressure is increased to 19 kbar. This is confirmed by the spectral evidence (Figure 17B). The spectral changes that occur when lauric acid solidifies are shown in Figure 18C which shows the result of subtracting the spectrum at 19 kbar from that at 14 kbar. This figure shows that major spectral changes occur when lauric acid solidifies. These changes include: a large (~20 cm^{-1}) low frequency shift of the 1720 cm^{-1} carbonyl vibration; loss of a 1750 cm^{-1} (C=O?) frequency; loss of intensity of the 1420 cm^{-1} frequency; a high frequency shift of the 1460 cm^{-1} CH_2 bending vibration; and gain in intensity of the 720 cm^{-1} CH_2 wag, the 880 OH bending mode, and the CH_2 rock-wags in the 1200-1300 cm^{-1} region.

Raising the pressure to 24 kbar produces small amounts of the same type of changes (Figure 18D) as seen when the sample solidifies (Figure 18C). However, when the sample (at 24 kbar pressure) is cooled from 100 C to a temperature below 65 C, only a small low frequency carbonyl shift can be detected (Figure 18E).

Figure 19 shows a spectrum of lauric acid at 19 kbar pressure and 100 C (Figure 19A) and a spectrum of lauric acid at 4 kbar pressure and 23 C (Figure 19B). Both samples are solids, but the spectra clearly indicate that Figures 19A and 19B represent different polymorphic forms. Note the differences at 1420, 1300, 940, and 880 cm^{-1}. Figure 19B represents the room temperature stable form while Figure 19A shows that at pressure and temperature, a different polymorph is produced.

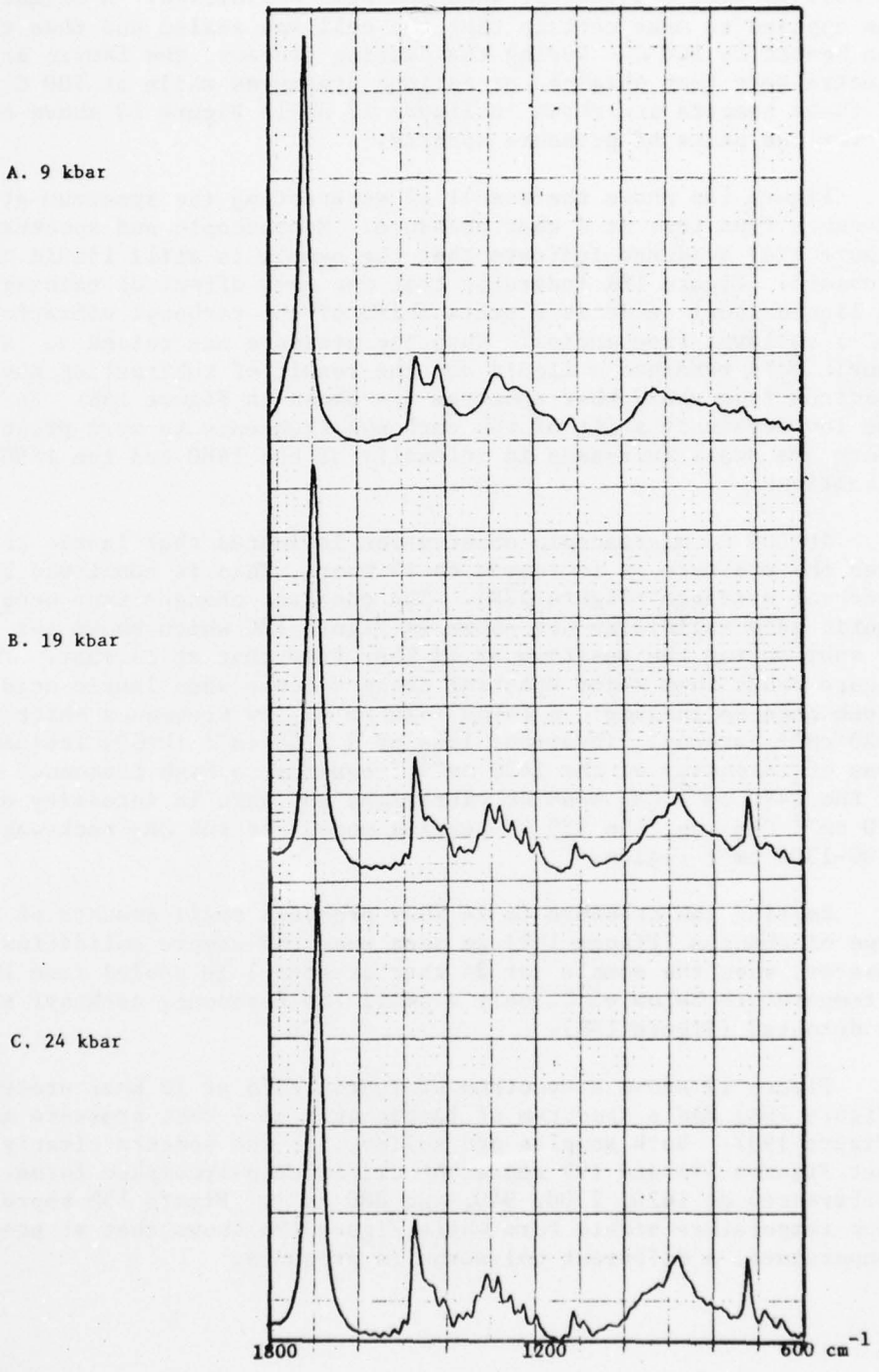


Figure 17. Infrared Spectra of Lauric Acid (100 C)

A. 4 kbar, 100 C
minus
9 kbar, 100 C

B. 9 kbar, 100 C
minus
14 kbar, 100 C

C. 14 kbar, 100 C
minus
19 kbar, 100 C

D. 19 kbar, 100 C
minus
24 kbar, 100 C

E. 24 kbar, 100 C
minus
24 kbar, <65 C

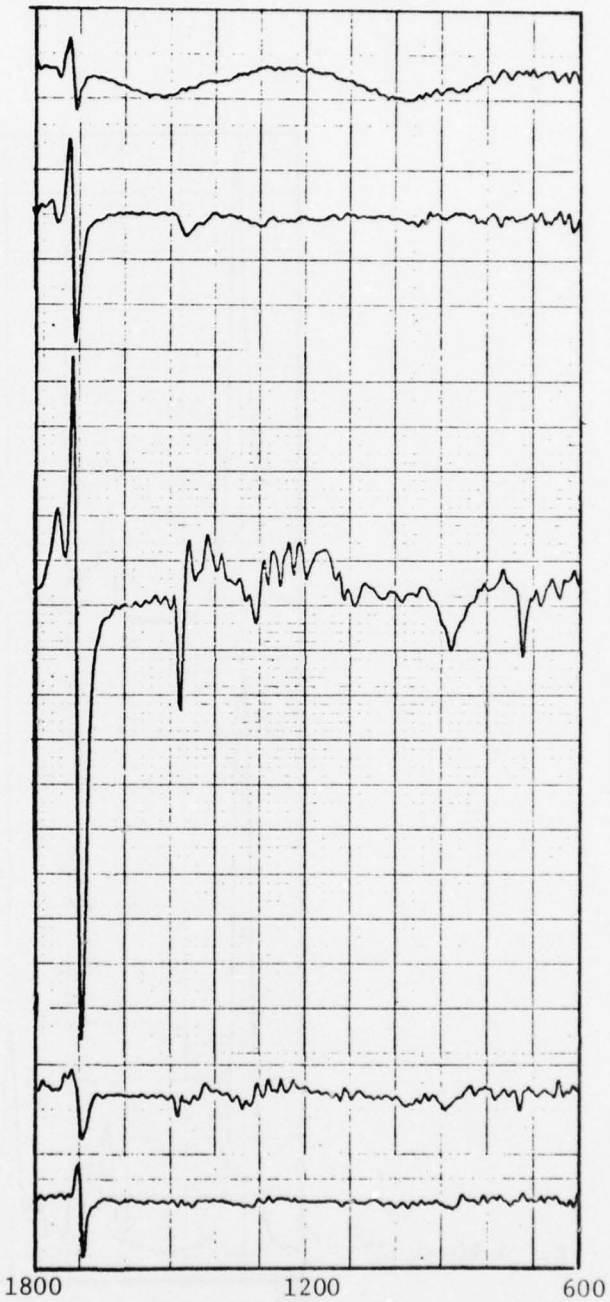


Figure 18. Subtracted Infrared Spectra of Lauric Acid

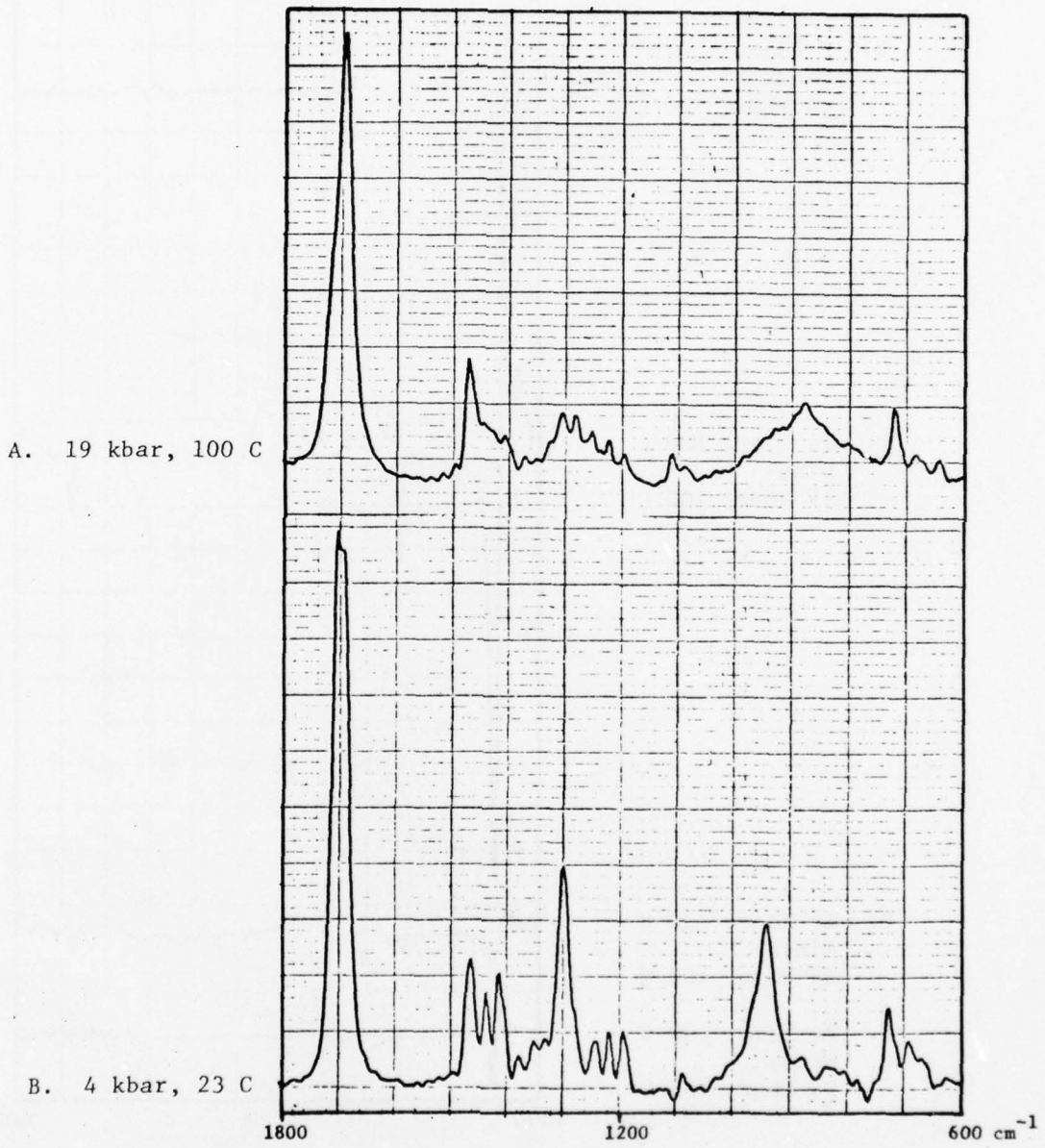


Figure 19. Infrared Spectra of Crystalline Lauric Acid

Solutions of Lauric Acid in Dodecane

Upon completion of the experiments on pure dodecane and pure lauric acid, a series of studies of solutions of these compounds was initiated. In these studies solutions varying from 1 through 10 net percent of lauric acid in dodecane were employed.

One Percent Solutions at Room Temperature. In the first set of experiments a 1 percent solution of lauric acid was loaded in the diamond cell and spectra were obtained at the same pressures used in the dodecane experiments (ambient to 34 kbar). Figure 20 shows the spectra at 1 atmos-p phere pressure for pure dodecane and the solution. As expected, the only difference is in the presence of a carbonyl band near 1715 cm^{-1}. At 10 kbar both microscopic and spectroscopic observation indicated that the sample was still liquid. At 14 kbar rapid and complete crystallization occurred. Raising the pressure to 24 kbar and then to 34 kbar caused no further visually observable phase changes. However, comparison of the spectra did show significant differences.

Figure 21A, the difference spectrum between 24 and 14 kbar, resembles the differences observed on going from liquid to solid solutions. Therefore, it can be concluded that even though the solution had apparently rapidly and completely crystallized at 14 kbar, some liquid solution remained or a "plastic" crystal phase had formed. Microscopic observation showed that the 1 percent solution crystallizes rapidly along two crystal axes but crystallizes very slowly along the third axis. Also, there is no change with pressure in the acid carbonyl vibration near 1715 cm^{-1}.

Figure 21B shows the difference spectra for 24 and 34 kbar pressure. In this spectrum all the CH vibrations are increasing in intensity as the pressure is increased. This is an indication that the solution was completely crystalline at 24 kbar. The acid carbonyl band (1715 cm^{-1}) appears to be losing intensity and possibly shows a frequency shift.

The difference between pure dodecane and the 1 percent solution are further delineated in Figure 22 which shows a pair of difference spectra between dodecane and the 1 percent solution at ambient pressure and at 24 kbar pressure. In Figure 22A false bands due to channelling are seen but the spectra do show perfect cancellation of the CH bands, leaving only the acid carbonyl band. Figure 22B, however, contains not only the carbonyl band but also all of the CH bands. Most significant here is that the patterns of the CH bands is similar to what is observed in going from liquid to solid dodecane indicating that the solution was less crystalline than pure dodecane.

The diamond anvil cell was again filled with fresh 1 percent solution and spectra were obtained at the same pressures as used in the dodecane studies (0, 10, 14, 24, 10R, 2R, 0R; where R signifies releasing pressure.) Slow solidification occurred at 10 kbar as in the case of pure dodecane. After 24 hours at 10 kbar, no further changes were observed. Figure 23

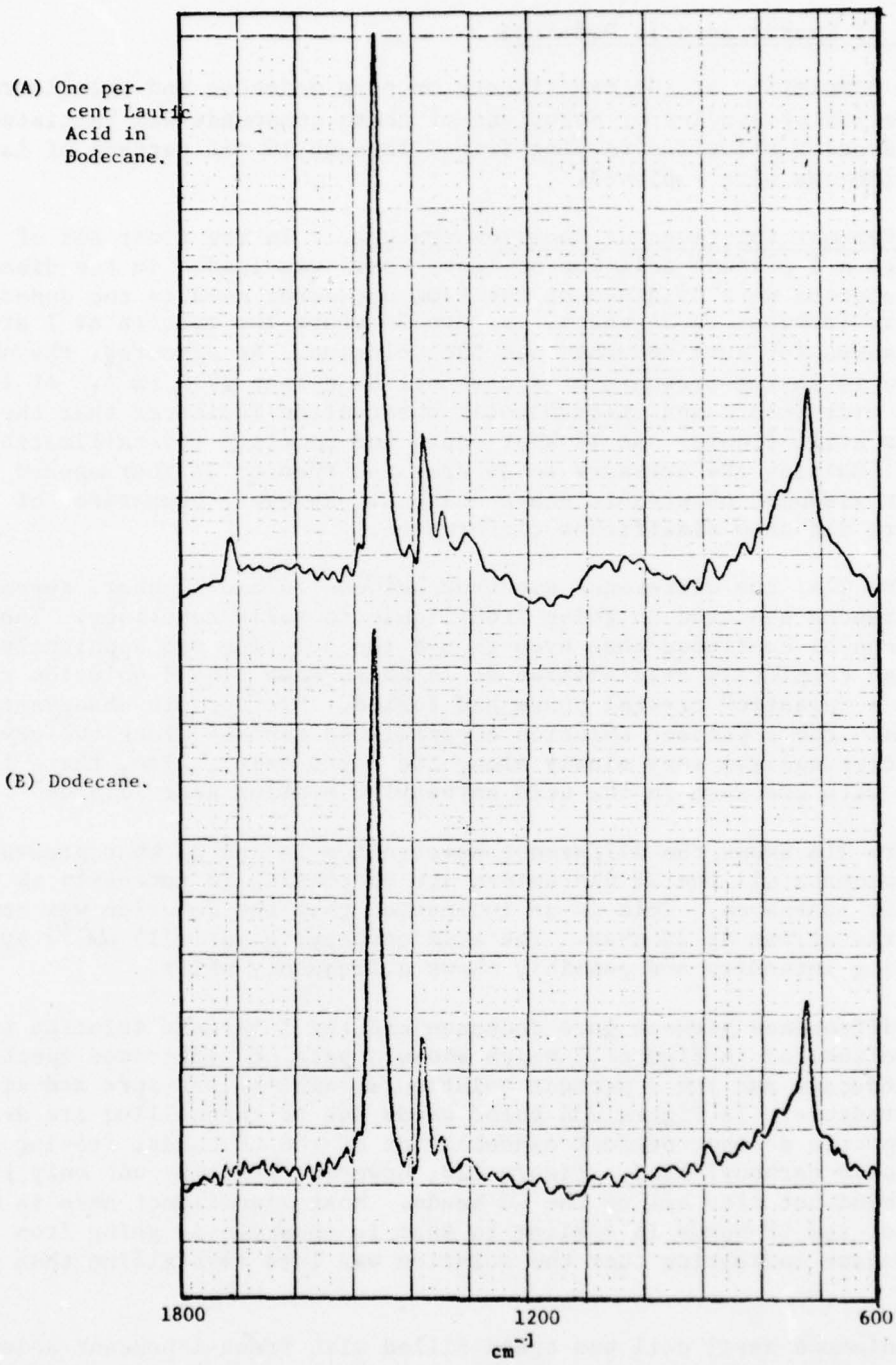


Figure 20. Infrared Spectra of Dodecane and One Percent Lauric Acid-Dodecane at Atmospheric Pressure

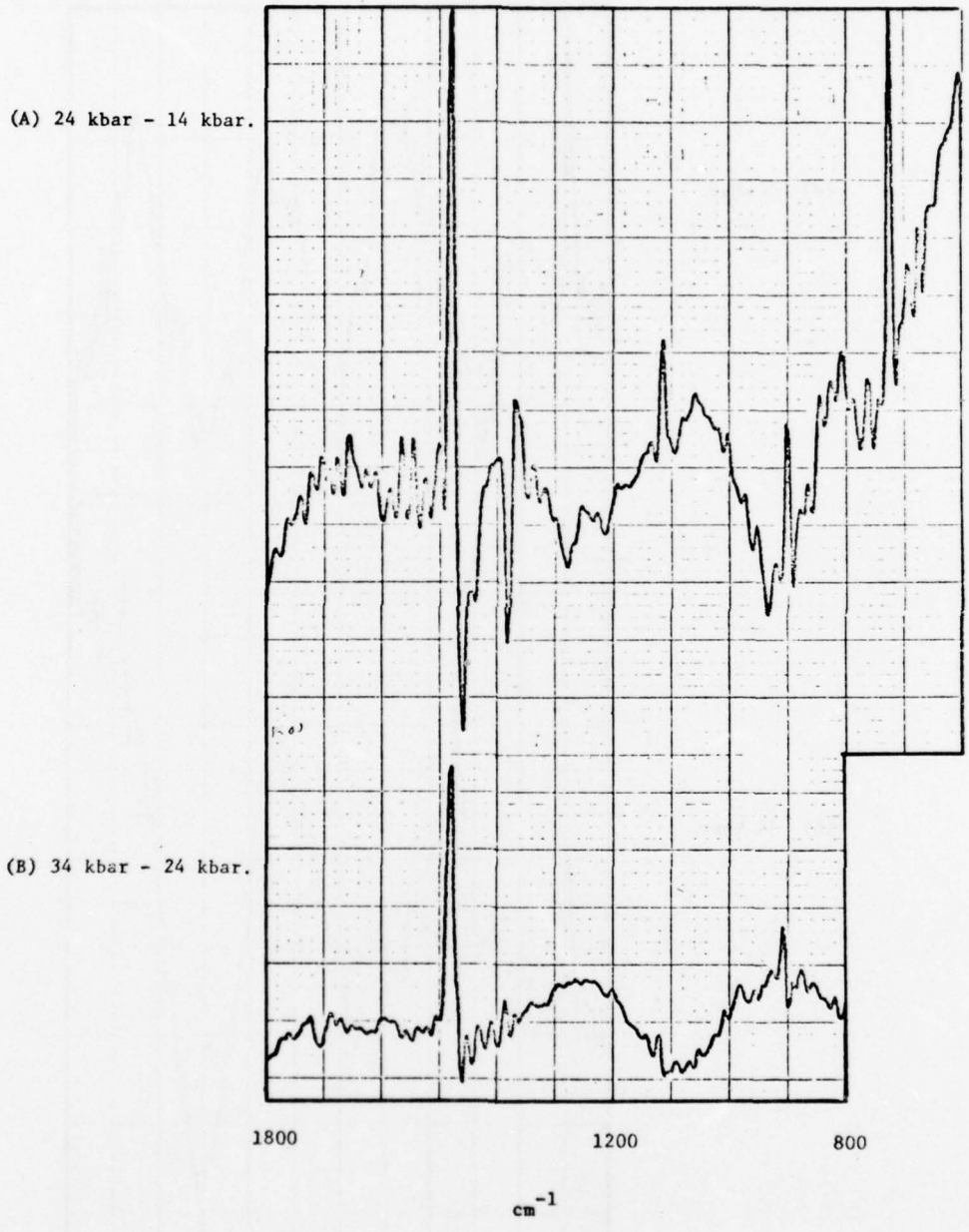


Figure 21. Subtracted Infrared Spectra of One Percent Lauric Acid in Dodecane (Subtractions of Spectra at Various Increasing Pressures)

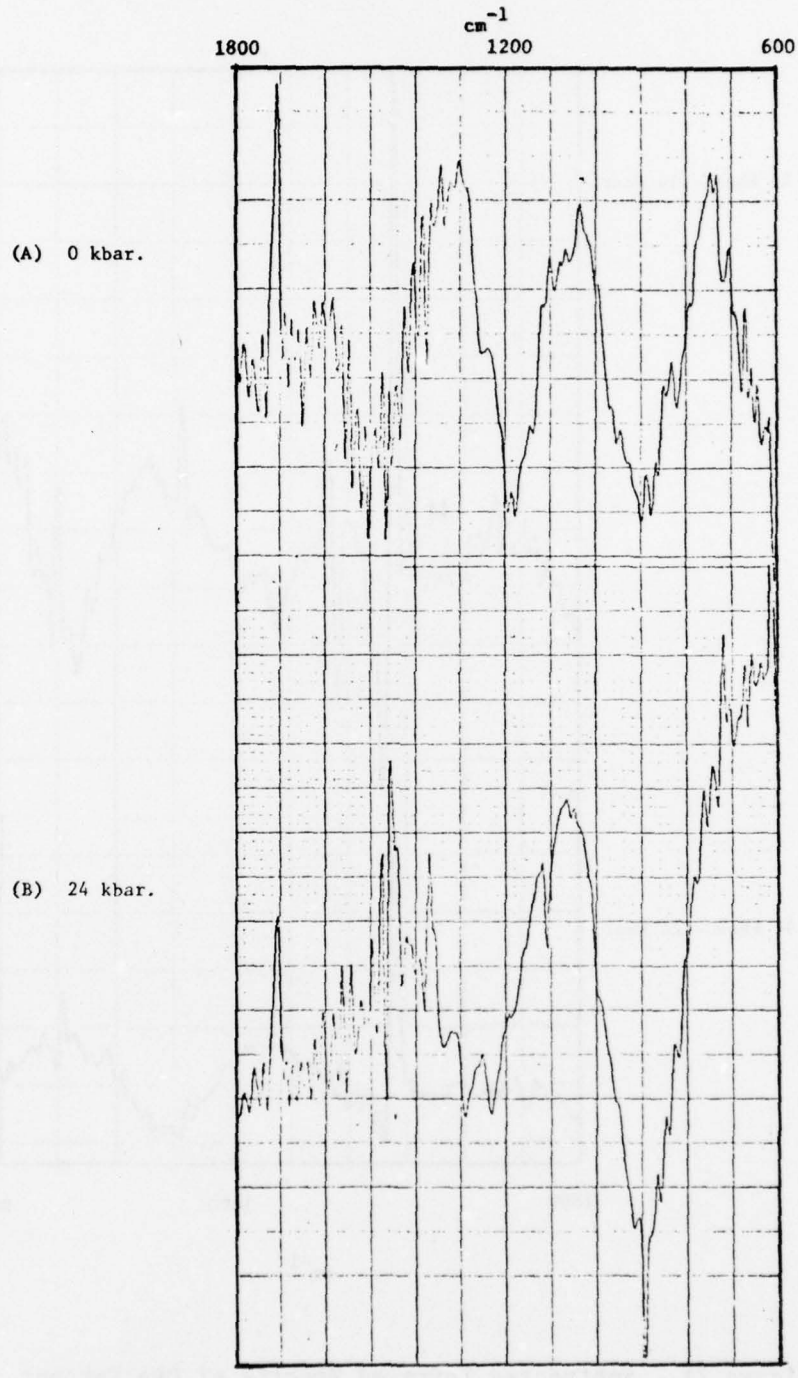
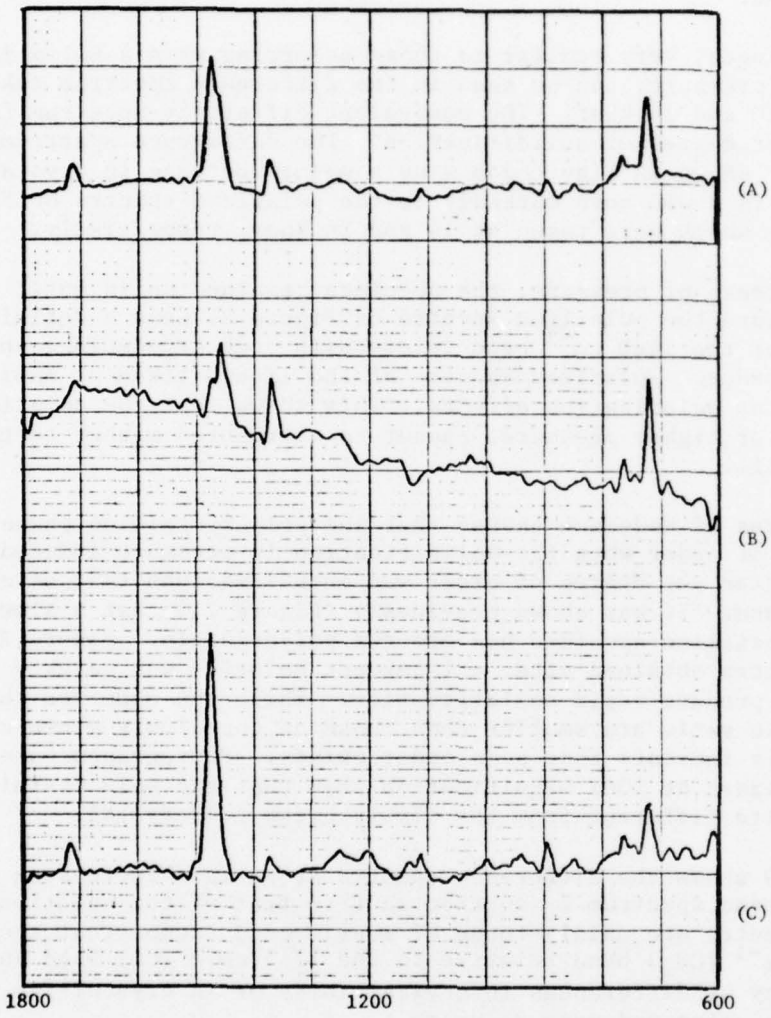


Figure 22. Subtracted Infrared Spectra of a One Percent Solution of Lauric Acid in Dodecane Minus Dodecane



(A) Nonpolarized
(B) Polarized - Polarizer at 45 C
(C) Polarized - Polarizer at 135 C

Figure 23. One Percent Lauric Acid-Dodecane Solution at 10 kbar

shows polarized and unpolarized spectra of the solution at 10 kbar. In the nonpolarized spectrum (Figure 24A), the bands near 890 and 1115 cm^{-1} indicates the presence of some crystalline material. The polarized spectra of Figure 22B and 22C indicate that some order exists but that the specimen is not a single crystal since the 1460 cm^{-1} bands are not completely split by polarization.

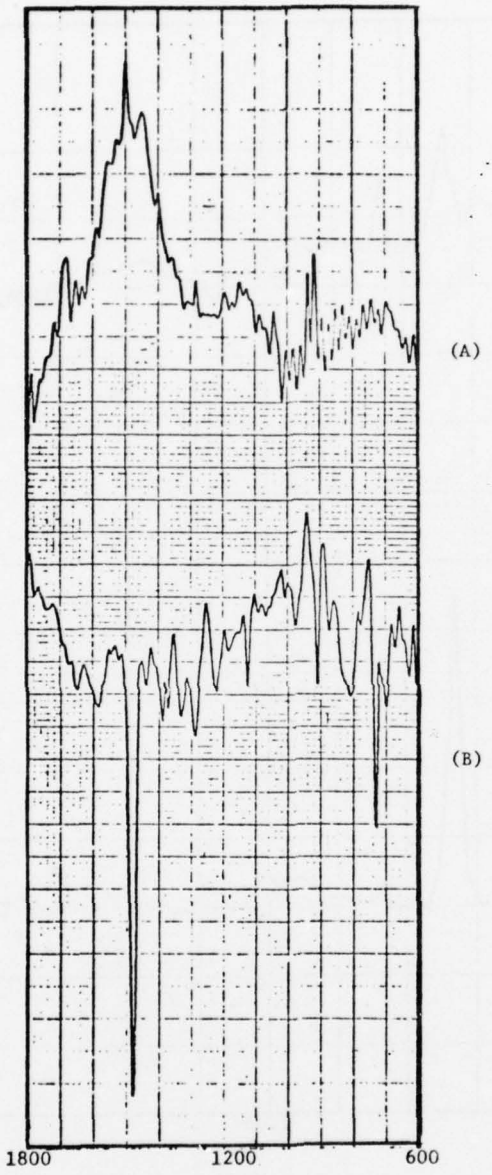
Small changes, very similar to those occurring when a solid is subjected to increasing pressure, can be seen in the difference spectrum taken between pressures of 10 and 14 kbar. The equivalent difference spectrum for dodecane showed a higher degree of solidification. The difference spectrum between 14 and 24 kbar shown in Figure 24B show a major increase in crystallinity. This increase is shown more markedly in the polarized spectra of Figure 25 and Figure 26, which were taken at 14 and 24 kbar, respectively.

Upon decrease of pressure, the specimen remained solid until about 2 kbar at which pressure the polarized spectra of Figure 27 show a definite change in the ratio of the 1460 cm^{-1} band (along with some broadening) indicating some loss of order. Polarized spectra of the liquid taken at ambient pressure show no polarization effects. This shows that the polarization effects noted at higher pressures cannot be attributed either to the instrument on the cell.

The studies of dodecane showed that the polycrystalline phase has a finite degree of order when the solidification is pressure-induced. As would be expected the degree of order was much less than that of single crystal dodecane. It was shown previously (Figure 24) that a slowly-grown polycrystalline specimen has ordered polycrystals. Figure 28 shows polarized spectra obtained after a 1 percent solution was quickly raised to 19 kbar to produce rapid solidification. While the observed changes in the dichroic ratio are smaller than those of the slowly-grown crystal, they definitely indicate that some order exists. Photographs taken under crossed polarizers at 100X magnification show that the polycrystal grown rapidly is quite different from the slowly grown polycrystal.

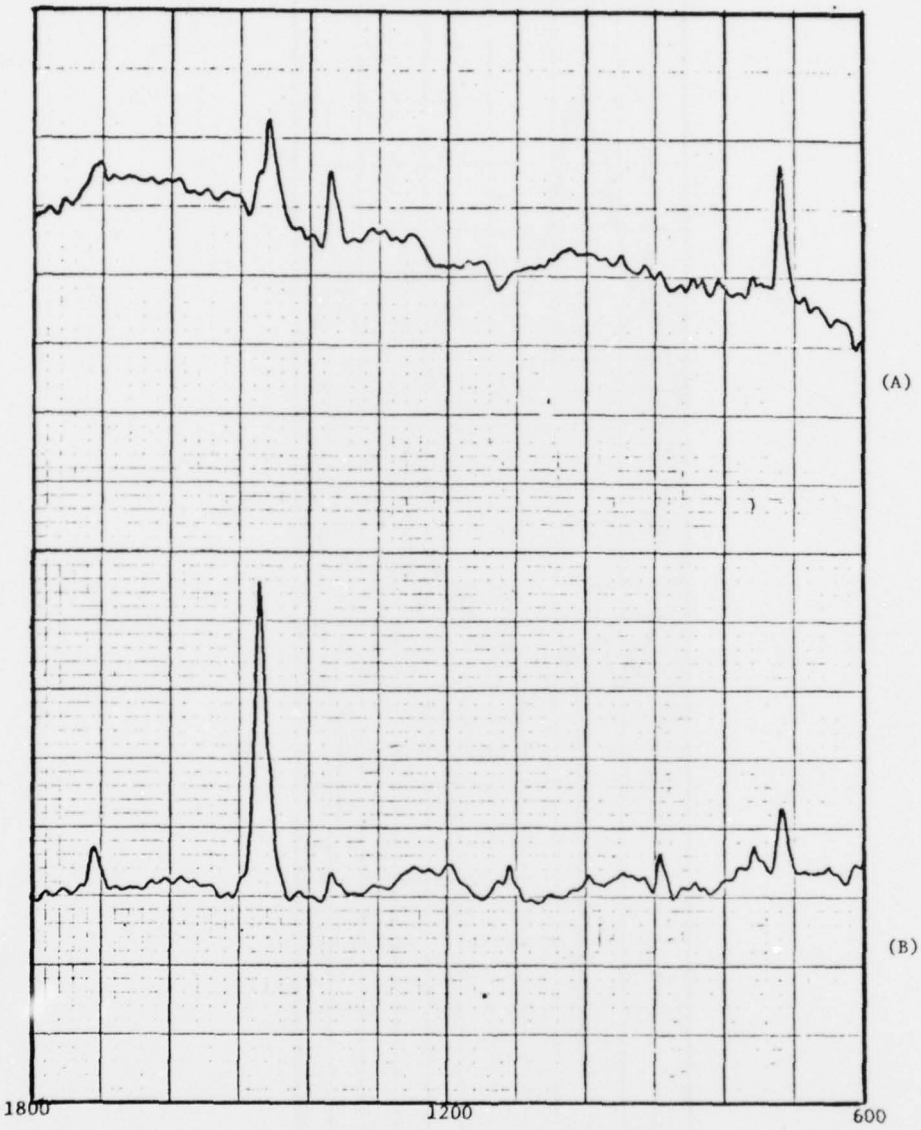
Figure 29 shows the difference spectra at various increasing pressures when the dodecane spectrum is subtracted from that of the solution. These difference spectra are mainly those of lauric acid except that the intensity of the 1460 cm^{-1} (CH_2) band relative to the 1715 cm^{-1} (CO) band indicates the possibility of differences in crystallinity or in crystalline phase between the solution and pure dodecane.

One Percent Solutions at Elevated Temperatures. A fresh 1 percent solution was placed in the diamond cell spectra were run at ambient pressure, and at 4 kbar pressure. The subtracted spectrum given in Figure 30 shows that there was virtually no change in the liquid from raising the pressure. The cell was then heated to 85 C at 4 kbar. The difference spectrum between 85 C and 23 C given in Figure 30B shows that heating results in major losses in band intensities for all infrared bands including the lauric acid carbonyl band.



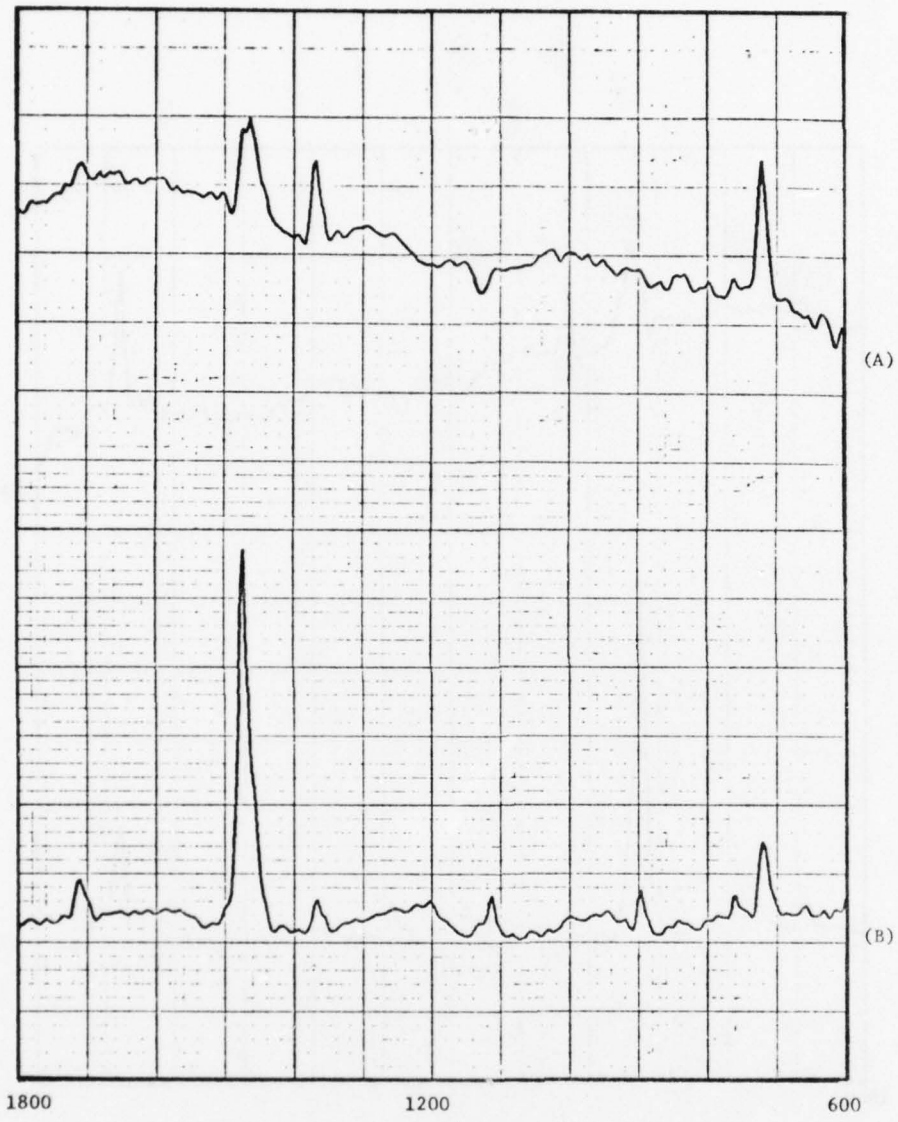
(A) 14 kbar - 10 kbar
(B) 24 kbar - 14 kbar

Figure 24. One Percent Lauric Acid-Dodecane Difference Spectra



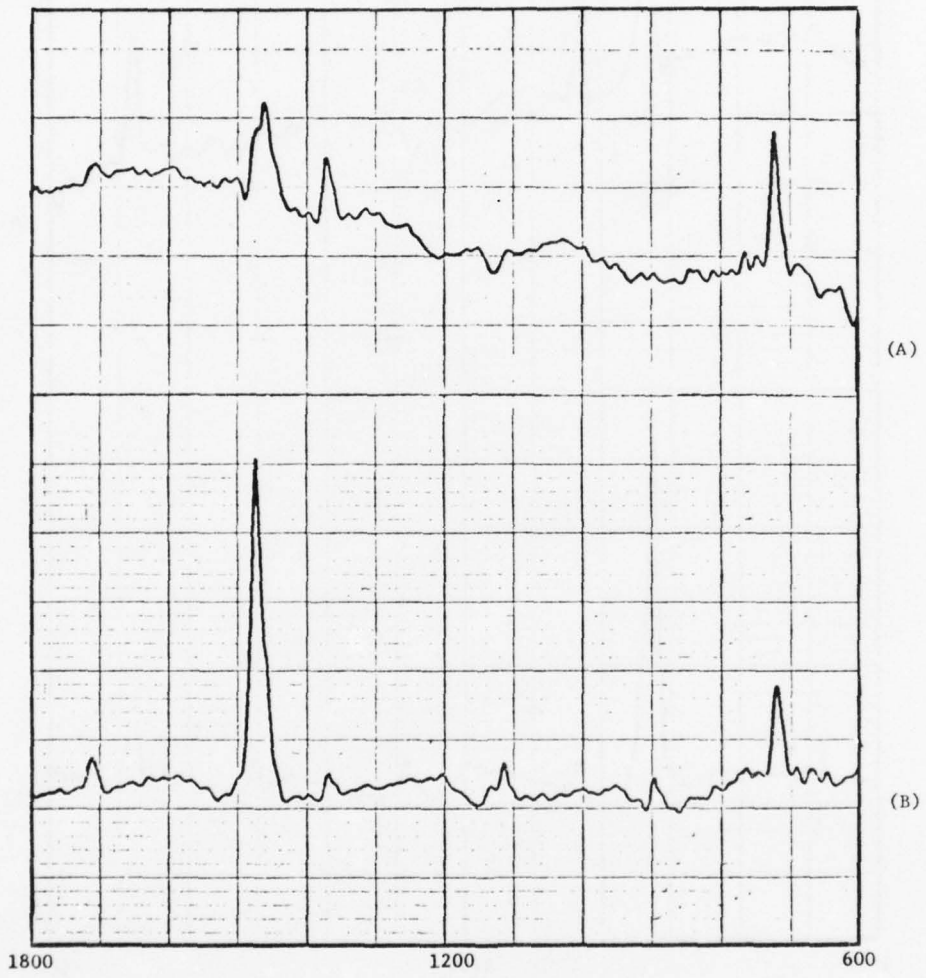
(A) Polarized Setting = 45 C
(B) Polarized Setting = 135 C

Figure 25. One Percent Lauric Acid-Dodecane at 14 kbar



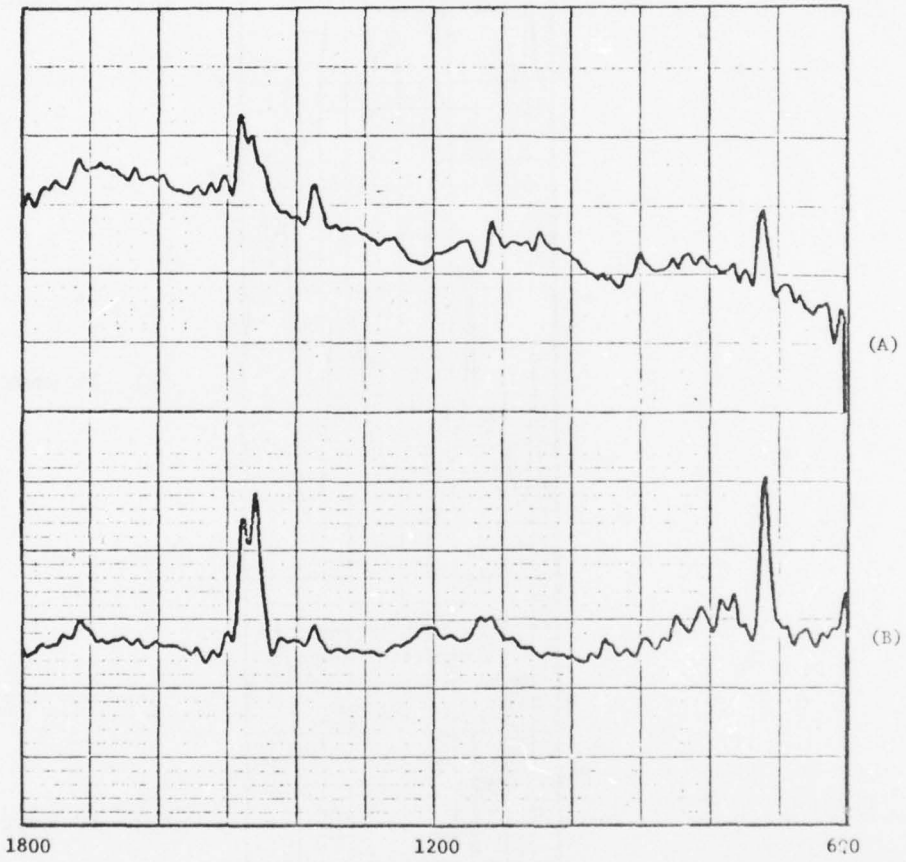
(A) Polarizer Setting = 45 C
(B) Polarizer Setting = 135 C

Figure 26. One Percent Lauric Acid-Dodecane at 24 kbar



(A) Polarizer Setting = 45 C
(B) Polarizer Setting = 135 C

Figure 27. One Percent Lauric Acid-Dodecane at 2 kbar (Releasing)



(A) Polarizer Setting = 45 C
(B) Polarizer Setting = 135 C

Figure 28. One Percent Lauric Acid-Dodecane at 19 kbar

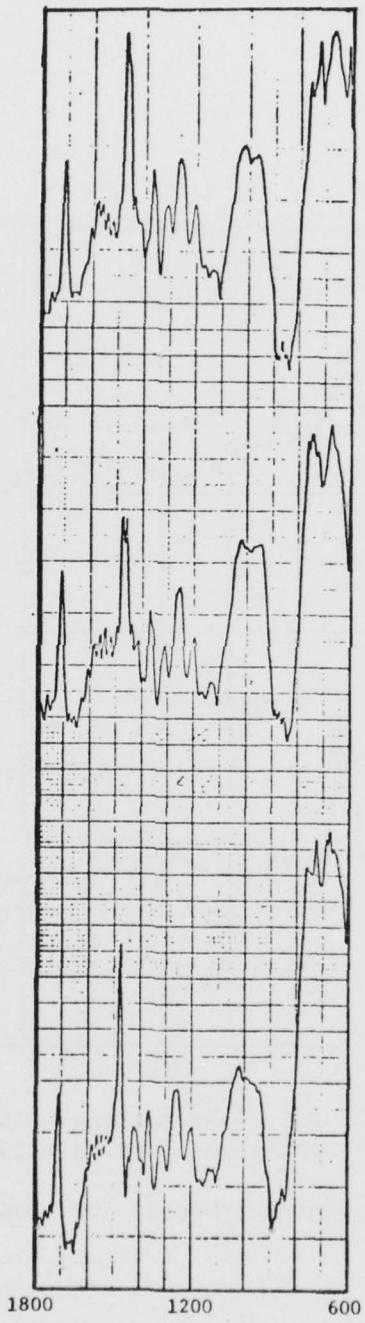


Figure 29. Difference Spectra Between One Percent Lauric Acid-Dodecane

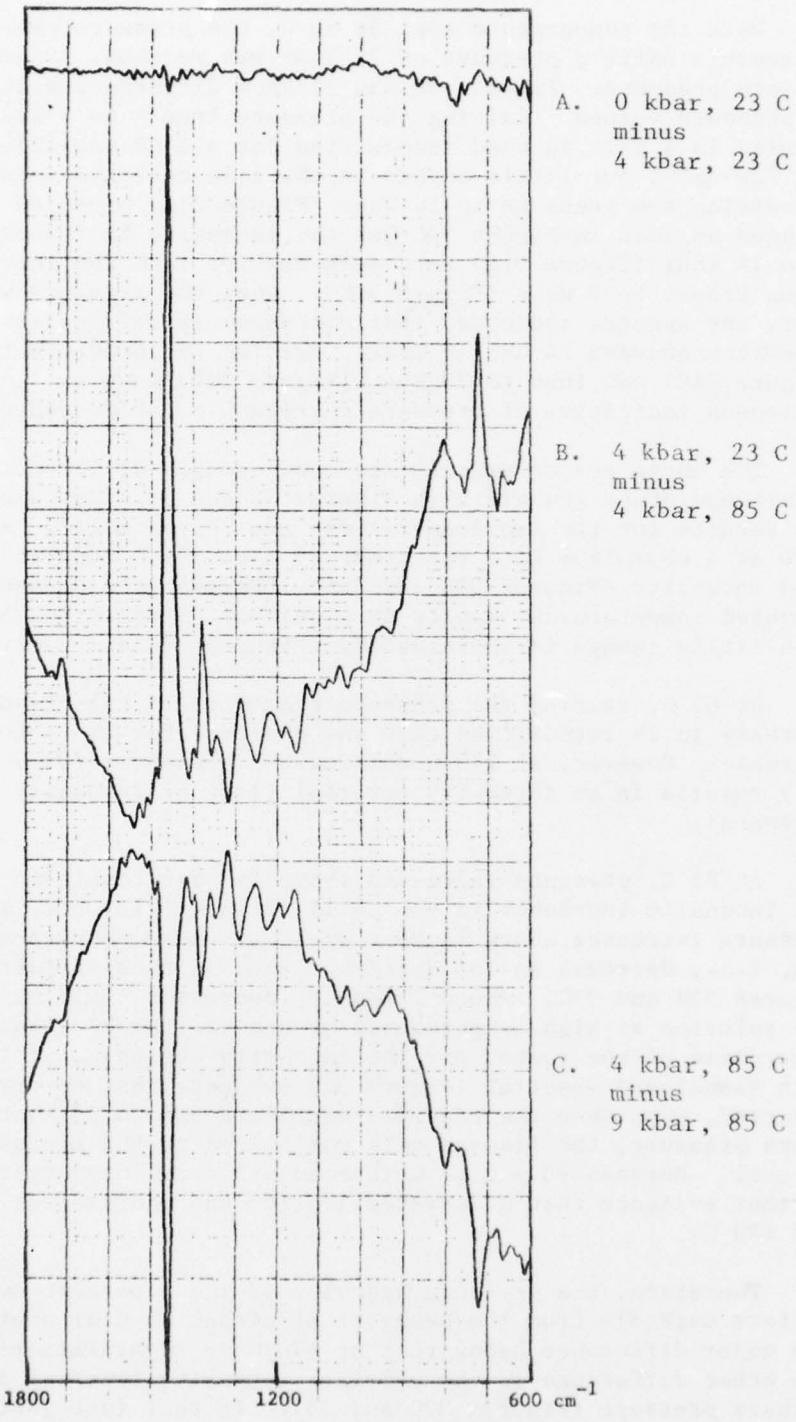


Figure 30. Subtracted Infrared Spectra of One Percent Lauric Acid in Dodecane

With the temperature kept at 85 C, the pressure was raised in 5 kbar increments until a pressure of 29 kbar was reached. Spectra were obtained at each pressure. Figures 30 and 31 show difference spectra between pairs of pressure values. Raising the pressure from 4 to 9 kbar (Figure 30C) results in a gain in band intensities for all CH vibrations (1460, 1380, and 720 cm^{-1}) but little change in the acid carbonyl intensity (1700 cm^{-1}). Increasing the pressure to 14 kbar (Figure 31A) produced the same type of changes as seen in Figure 30C but the intensity increases on going from 9 to 14 kbar (Figure 31A) were much smaller than the intensity changes on going from 4 to 9 kbar (Figure 30C). When the pressure was raised to 19 kbar, the spectra indicated that dodecane crystallization had occurred somewhere between 14 and 19 kbar. Raising the pressure from 19 to 24 kbar (Figure 31C) and then to 29 kbar (Figure 31D) gave small IR intensity increases indicative of pressure increases on solid dodecane.

The above set of experiments was repeated at 170 C. The results at this temperature are given in Figures 32 and 33. Up to a pressure of 9 kbar, the results for the two temperatures are very similar. Raising the temperature at 4 kbar from 23 C to either 85 C or 170 C results in a loss of IR band intensity (Figures 30B and 34B). Raising the pressure at these elevated temperatures results in a gain of CH vibration band intensities with little change in CO intensity (Figures 30C and 34C).

At 85 C, raising the pressure from 9 to 14 kbar resulted in a smaller increase in IR intensities than was observed for the 4 to 9 kbar pressure increase. However, at 170 C raising the pressure from 9 to 14 kbar (Figure 33A) results in an intensity reversal (loss of intensity with increasing pressure).

At 85 C, pressure increases above 14 kbar result in crystallization and intensity increases in the solid (Figures 31B, 31C, and 31D). At 170 C, pressure increases above 14 kbar yield the same results as shown in Figure 33A, i.e., decrease in intensities. Some of these results are shown in Figures 33B and 33C. These intensity decreases could be due to changes in the solution at high temperatures or due to loss of solution from the cell. Regardless of the reason for the intensity decrease, it is conclusive from both visual and spectral (Figure 33) evidence that no crystallization has occurred, even when the pressure was increased to 39 kbar. While at 39 kbars pressure, the diamond cell was placed in the microscope and allowed to cool. Between 70 and 67 C, the solution rapidly crystallized, which is further evidence that no crystallization had occurred at 39 kbar pressure and 170 C.

Therefore, the pressure behavior of the 1 percent solution at 170 C differs markedly from the behavior at either 85 C or ambient temperature. The major difference being that at 170 C no crystallization occurred. The other difference is the possible intensity reversal at 170 C and over 9 kbars pressure (Figures 32C and 33). If real (not just due to loss of solution), this could be significant and indicating a structural change due to temperature and pressure.

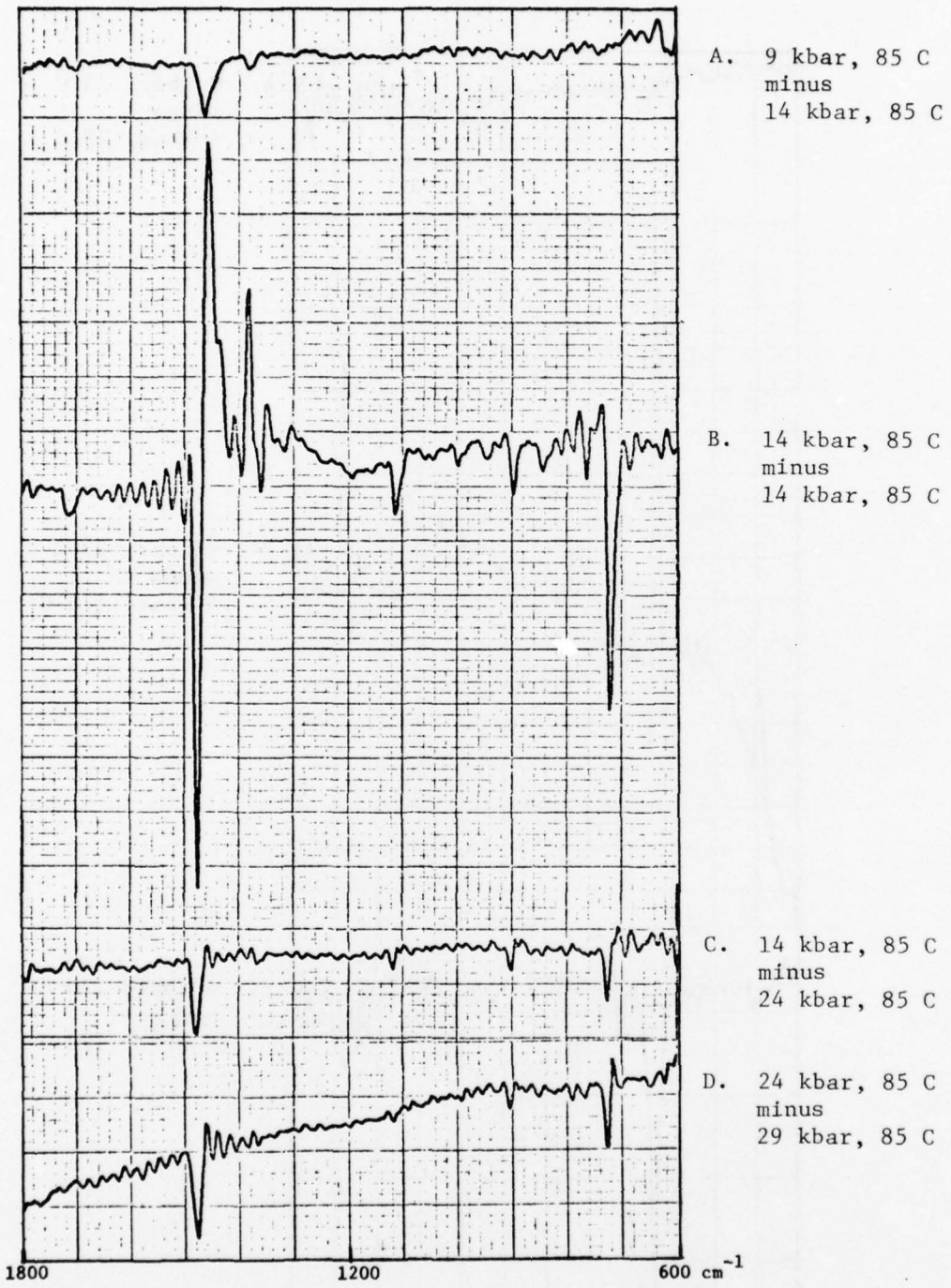


Figure 31. Subtracted Infrared Spectra of One Percent Lauric Acid in Dodecane

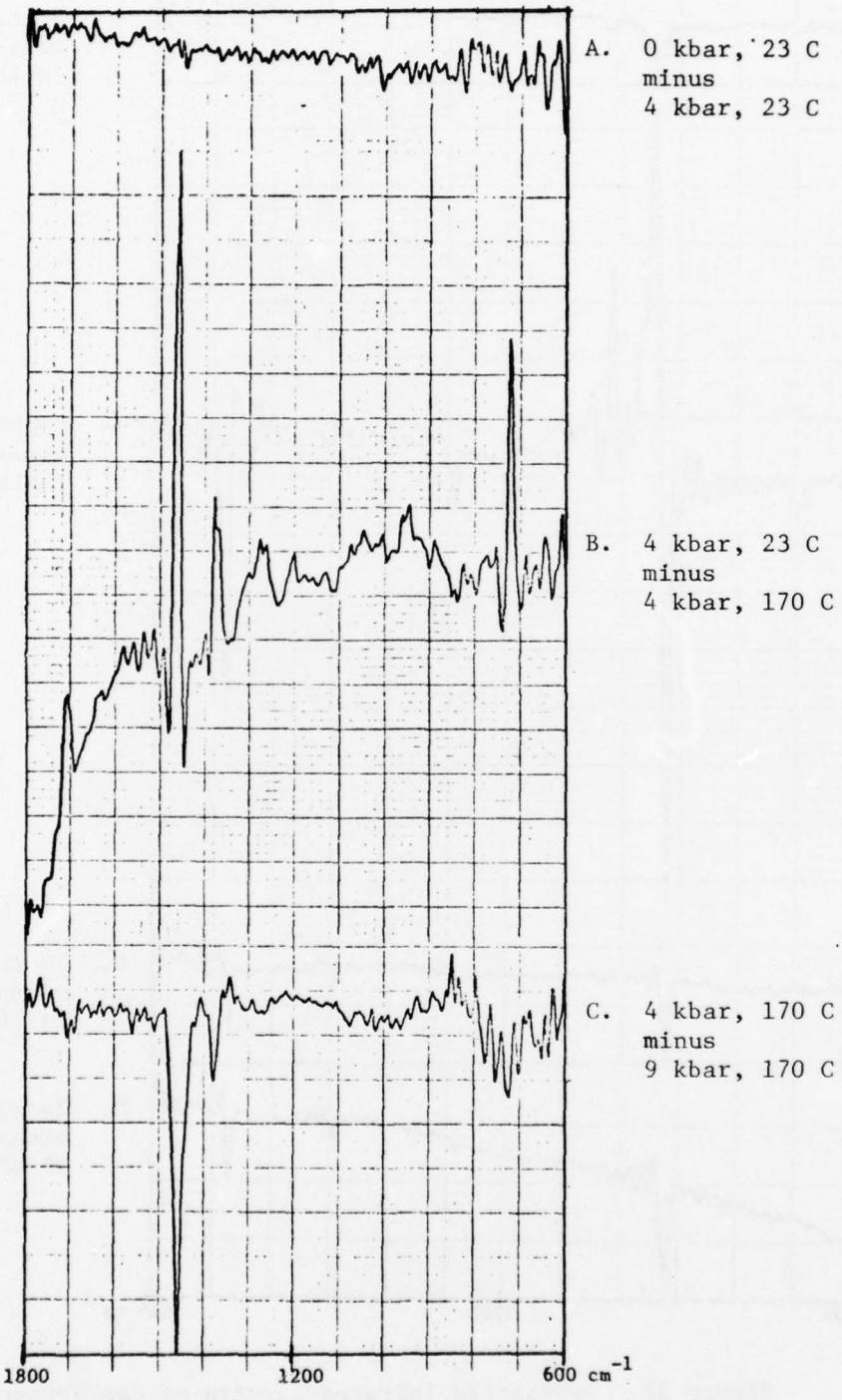


Figure 32. Subtracted Infrared Spectra of One Percent Lauric Acid in Dodecane

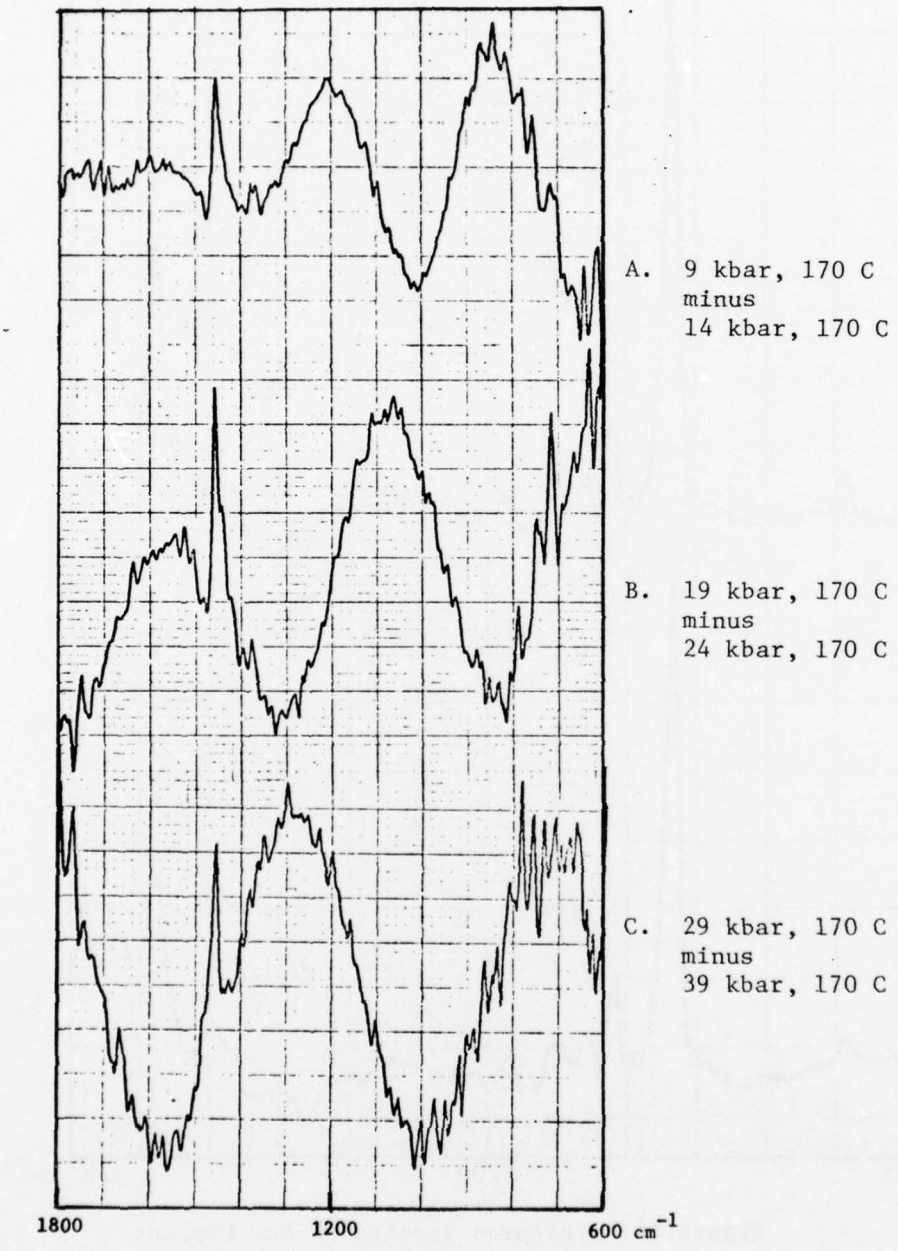


Figure 33. Subtracted Infrared Spectra of One Percent Lauric Acid in Dodecane

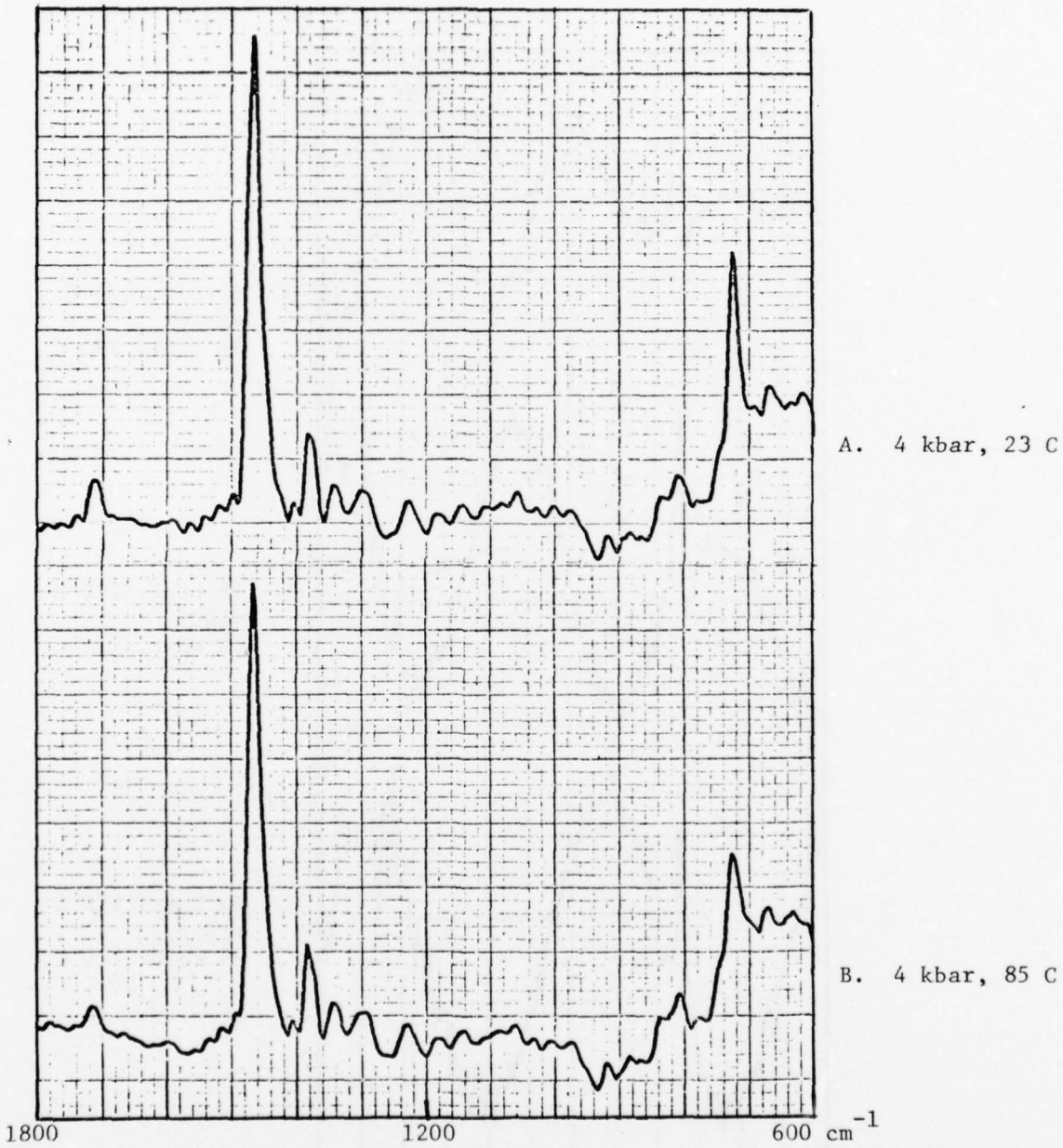


Figure 34. Infrared Spectra of One Percent Lauric Acid in Dodecane

Previously we had noted that one difference between heating a 1 percent solution to 85 C and heating the solution to 170 C was in the change in intensity of the carbonyl (1700 cm^{-1}) vibration of lauric acid. This is illustrated in Figures 34 and 35. Figure 34A shows the spectrum of a 1 percent lauric acid-dodecane solution at 4 kbar pressure and at 23 C. Figure 34B shows the spectrum of this solution (4kbars pressure) after heating to 85 C. Here it can be seen that the effect of heating this solution to 85 C is to decrease the carbonyl band intensity, but the band does not disappear.

Figure 35A also shows the spectrum (2X expanded compared to Figure 34) o a 1 percent lauric acid-dodecane solution at 4 kbar pressure and at 23 C. The spectrum of this solution after heating to 170 C is shown in Figure 36. At 170 C there is no evidence for a carbonyl vibration (at least to the limits of our detectability). This loss of intensity of the carbonyl vibration at 85 C and at 170 C can also be seen in the subtracted spectra of Figures 30B and 32 B.

Five Percent Solution. A series of experiments showed that a 5 percent solution of lauric acid in dodecane shows the same behavior as a 1 percent solution when the pressure is increased. That is, crystallization began at 10 kbar but was not complete until the pressure reached 15 kbar. This is shown in the difference spectra of Figures 37A and 37B. However, the spectra obtained upon releasing the pressures show significant differences between the 1 percent and 5 percent solutions. Figure 37C, the difference spectrum between 15 kbar (releasing) and 10 kbar releasing shows evidence for partial melting. The equivalent spectra for the 1 percent solution showed only loss of crystallinity and did not show melting changes. The partial melting becomes more evident in Figure 37D which shows the result of subtracting the 10 kbar (releasing) spectrum from the 3 kbar (releasing) spectrum. Thus, the 5 percent solution shows partial melting upon release of pressures, whereas the 1 percent solution showed only loss of crystallinity until it completely melted at about 1 kbar.

The polarized spectra of the 5 percent solution at 10 kbar presented in Figure 38 emphasize these changes. The polarization splitting of the 1460 cm^{-1} band (CH_2 bending) indicates order in the polycrystalline phase. On the other hand, when the pressure is released to 15 kbar, there is almost no splitting of the 1460 cm^{-1} band (Figure 39). Some small dichroic effects are still seen in the 1375 cm^{-1} band indicating some degree of order but this is far less than observed in the polarized spectra of the 1 percent solution.

Ten Percent Solution. A 10 percent solution of lauric acid in dodecane was placed in the diamond window high pressure cell using a 1 mil platinum gasket. Infrared spectra were obtained at ambient pressure, at 5 kbar, and

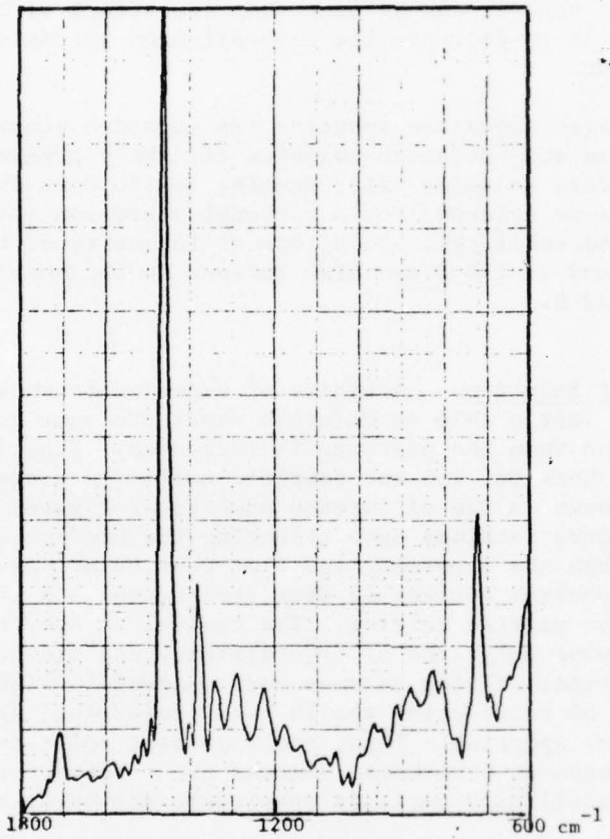


Figure 35. Infrared Spectra of One Percent Lauric Acid in Dodecane at 4 Kbar (23 C)

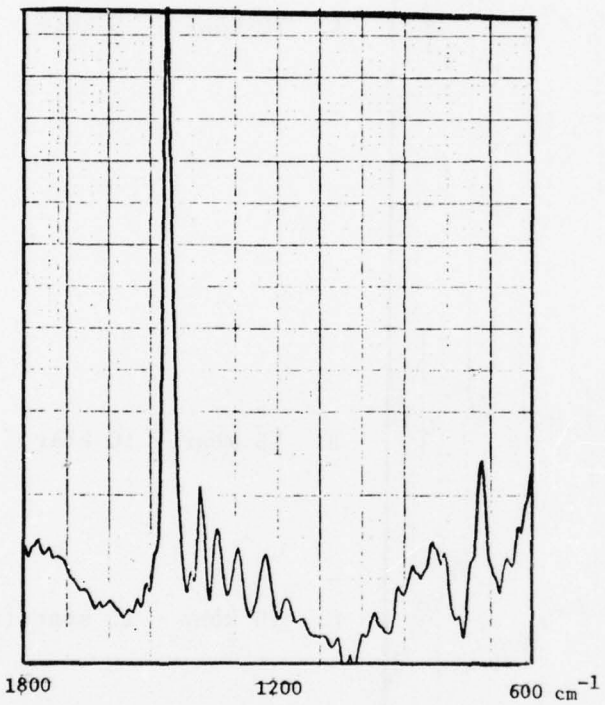
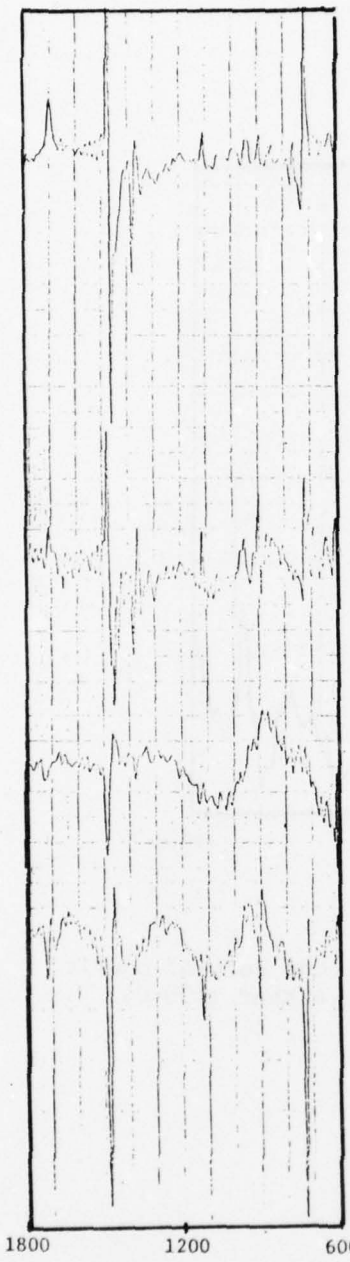


Figure 36. Infrared Spectra of One Percent Lauric Acid in Dodecane at 4 Kbar (170 C)



A. 10 kbar - 5 kbar

B. 15 kbar - 10 kbar

C. 10 kbar - 15 kbar (releasing pressure)

D. 3 kbar - 5 kbar (releasing pressure)

Figure 37. Subtracted Infrared Spectra (5 Percent Lauric Acid in Dodecane at Various Pressures)

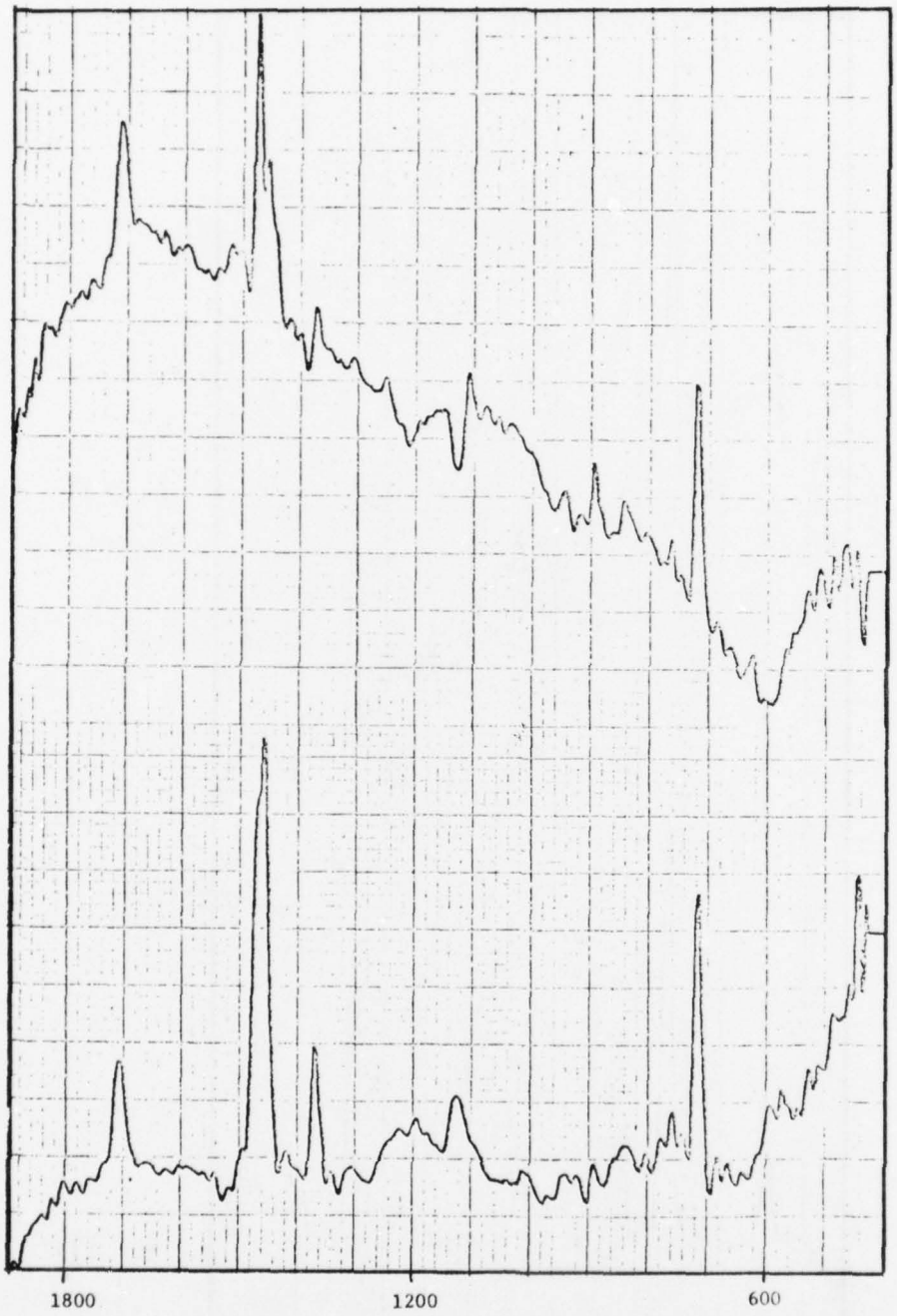


Figure 38. Polarized Infrared Spectra of 5 Percent Lauric Acid in Dodecane at 10 Kbar

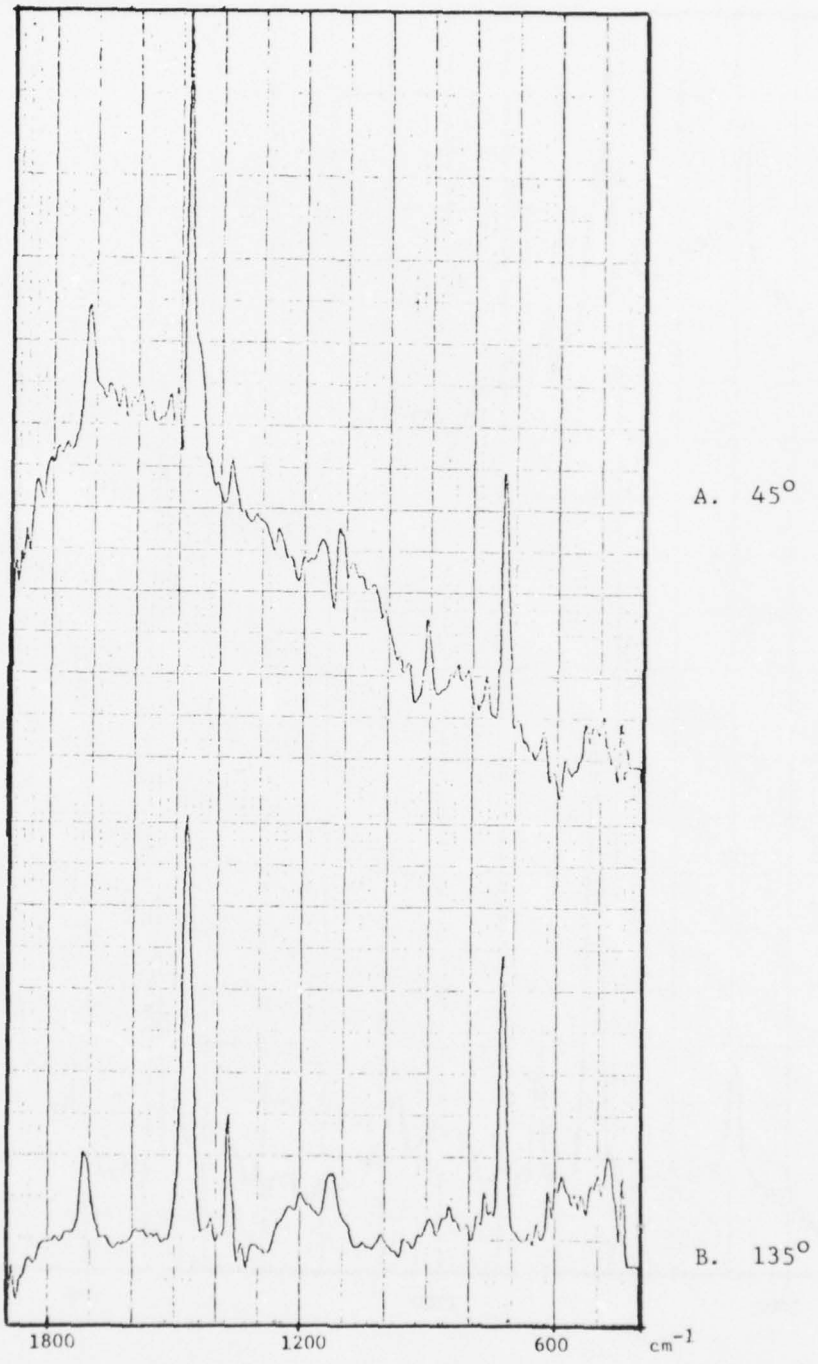


Figure 39. Polarized Infrared Spectra of 5 Percent Lauric Acid in Dodecane at 15 Kbar (Releasing Pressure)

at 10 kbar pressure. Both the visual observations (through a microscope) and the spectral changes indicated that the solution was still liquid at 10 kbar. This solution was allowed to stand at 10 kbar pressure for 70 hours, after which infrared spectra were again obtained. Subtraction of the 10 kbar, 0 hours spectrum from the 10 kbar, 70 hours spectrum gave the results shown in Figure 40A. This result shows an increase (with time) in intensity of the carbonyl vibration (1715 cm^{-1}) and a broadening of the CH_2 wag-rock frequency near 720 cm^{-1}.

The pressure was then raised to 14 kbar, and Figure 40B shows the result of subtracting the 10 kbar, 70 hours spectrum from the 14 kbar, 0 hours spectrum. Here the changes are an increase in intensity of the 1715 cm^{-1} carbonyl vibration and an increase in intensity of the 1465 cm^{-1} CH_2 bending vibrations. The change in the 1465 cm^{-1} frequency is characteristic of pressure induced changes in the liquid hydrocarbon and indicate that the changes illustrated in Figure 40A may not be due to pressure changes since there is no change in the 1465 cm^{-1} band (Figure 40A).

The solution was allowed to stand at 14 kbar applied pressure for 88 hours with spectra being taken intermittently during this period. At 0 and 16 hours both the visual and spectroscpic observations indicated that the solution was a liquid. Figure 40C shows the results of subtracting the 14 kbar, 0 hours spectrum from the 14 kbar, 16 hours spectrum. Even though the sample is still liquid, major spectroscopic changes can be observed, i.e., a low frequency shift of the carbonyl frequency along with intensification of the 1465 and 770 cm^{-1} bands. The magnitude of these changes strongly indicate that the possible slight increase in pressure (due to gasket compression) cannot account for all of the changes (compare Figure 40C with Figures 40A and 40B).

After standing at 14 kbar for 20 hours, visual observation indicated the presence of a small crystal. Subtraction of the 14 kbar, 16 hours spectrum from that of 14 kbar, 20 hours, however, showed no spectral differences (Figure 40D). This is a further clue that the changes in Figure 40C cannot be due to pressure alone. At 21 hours, the crystal had grown by three-four fold (photomicrograph shown in the lower right hand corner of Figure 41). In this photomicrograph, the crystal is the rod-like shape in the upper portion of the cell running from northeast to southwest. The oval object in the upper right hand portion of the cell is a piece of debris and is neither lauric acid or dodecane. Subtraction of the 14 kbar, 20 hours spectrum from that of 21 hours at 14 kbar gave the results shown in Figure 40E. These changes (low frequency shift of 1715 cm^{-1} carbonyl and increase in intensity of 1465 cm^{-1} CH_2 bend) likely result from the increase in the amount of crystal in the solution. Note that these are large changes as compared to Figure 40D and are similar to the changes observed in Figure 40C (changes in liquid with time). This could indicate an important fact - that at an elevated but constant pressure, structuring changes are occurring in the liquid and these changes are similar to the changes observed as the liquid crystallizes. In other words, the structure of the liquid, near the crystallization point, approximates

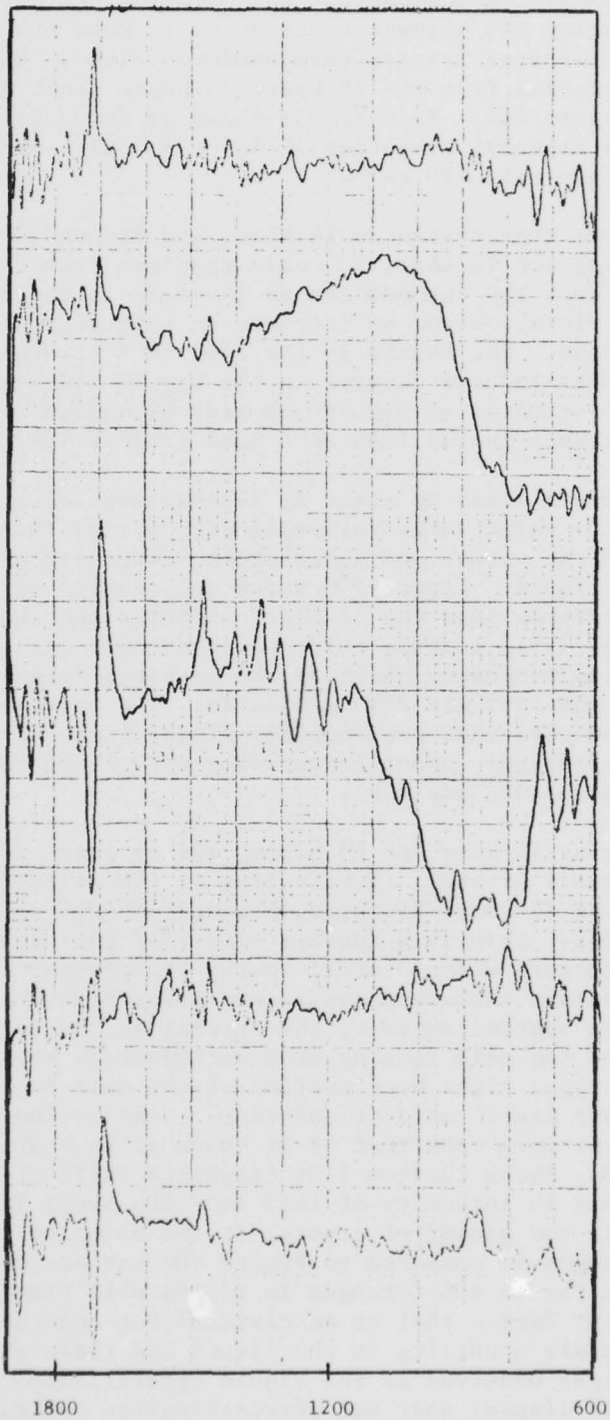


Figure 40. Subtracted Infrared Spectra (10 Percent Solution of Lauric Acid in Dodecane)

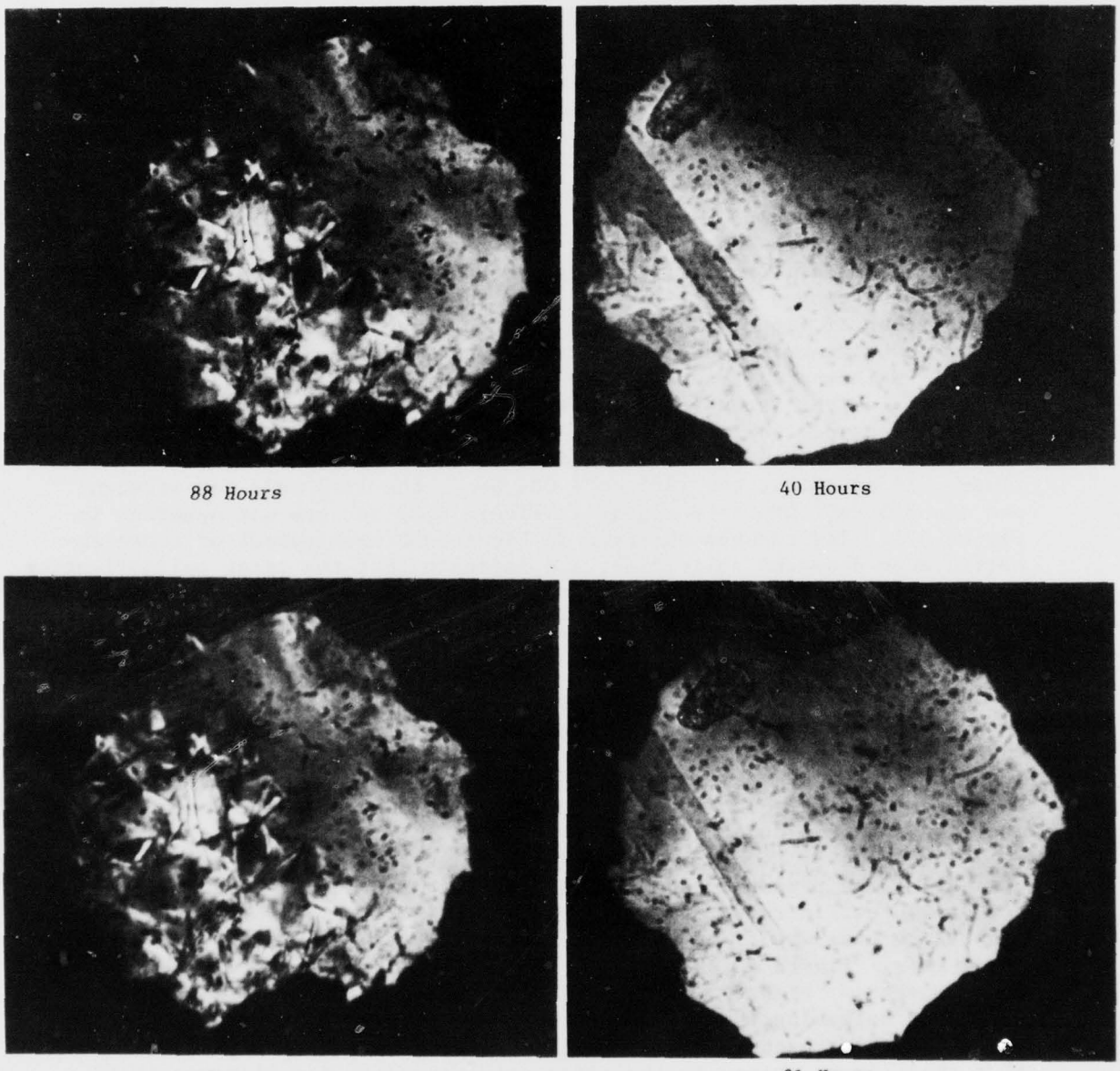
that of the crystal. The only alternative explanation is that at 16 hours at 14 kbar a crystal is present which is not visual under the microscope. If reproducible, these experimental observations can have important consequences in boundary lubrication behavior.

The crystal slowly increased in size, but by 40 hours at 14 kbar, no further growth could be detected. A photomicrograph taken at 40 hours is shown in the upper right hand corner of Figure 41 and the result of subtracting the 21 hours spectrum from the 40 hours spectrum is shown in Figure 40. The spectral changes observed between 21 and 40 hours are the same type as observed (in Figure 40E) between 20 and 21 hours. It is of interest to note that polarized spectra (not shown) obtained at 21 hours show no dichroic effects, i.e., show no signs of long range order.

At 45 hours, a polycrystalline mass formed in the remainder of the cell (photomicrograph in the lower left hand corner of Figure 41). This polycrystalline mass is even more apparent (because of different microscope polarizer settings) in the photomicrograph taken at 88 hours (upper left hand portion of Figure 41). The subtracted spectra between 45 and 40 hours and between 88 and 45 hours are shown in Figures 42B and 42C, respectively. Note the differences between Figures 42A and 42B. In Figure 42B, there is a slight intensity increase in the 1715 cm^{-1} carbonyl band, but not the frequency shift as seen in Figure 40A. Also, there are major differences (between Figure 42A and 42B) in the 1465 and 720 cm^{-1} vibrations. In addition, the 1385 cm^{-1} CH_3 bend, the 1118 cm^{-1} C-C stretch, and the 895 cm^{-1} CH_3 rock appear in Figure 42B, but are not apparent in Figure 42A. The changes observed in Figure 42B are typical of those observed when dodecane solidified, and indicate that the first solidification observed (20 to 40 hours) was solidification of lauric acid. Polarized spectra taken at 45 hours (not shown) still show no dichroic changes, thus, no indications of long range order.

Figure 42C gives very little indication of any changes, thus demonstrating that solidification was essentially complete after 45 hours at 14 kbar. The pressure was then raised to 24 kbar and Figure 42D shows the result of subtracting the 88 hour at 14 kbar spectrum from that at 24 kbar. Here the slight increase in intensity of all bands is typical of pressure increase on solid dodecane.

After the pressure had been increased to 24 kbar, we began to release the pressure. Infrared spectra were obtained at the following pressures (releasing pressure): 14 kbar; 10 kbar, 0 hours; 10 kbar, 64 hours; 5 kbar; and 4 kbar. Figure 43 shows the results of subtracting various pairs of these spectra. Figures 43A and 43B show that there is no detectable spectral change on releasing the pressure from 24 to 14 kbar (Figure 43A) or on releasing the pressure from 14 to 10 kbar (Figure 43B). Figure 43C shows that there is no change in the solid after standing for 64 hours at 10 kbar.



88 Hours

40 Hours

45 Hours

21 Hours

FIGURE 41. PHOTOMICROGRAPHS, 10 PERCENT LAURIC ACID IN DODECANE AT 14 KBAR PRESSURE

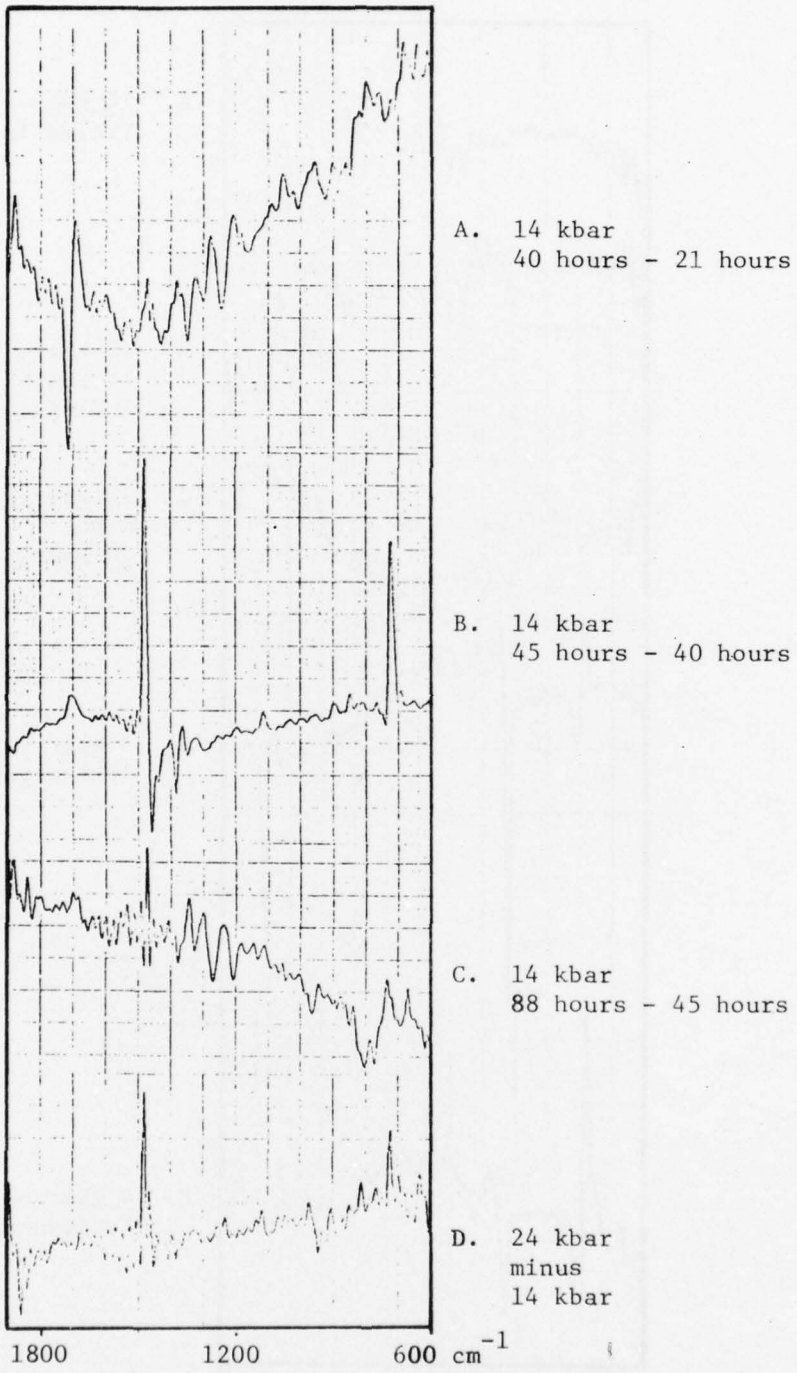


Figure 42. Subtracted Infrared Spectra (10 Percent Solution of Lauric Acid in Dodecane)

Figure 43. Subtracted Infrared Spectra (10 Percent Solution of Lauric Acid in Dodecane) Decreasing Pressure

However, Figure 43D shows the results of subtracting the 5 kbar spectrum from the 10 kbar spectrum (as pressure is being released) and indicates that the dodecane is melting and some of the lauric acid is melting (confirmed by microscopic observations). Upon releasing the pressure to 4 kbar, all of the sample melts and the spectral differences (Figure 43E) indicate this melting. Furthermore, Figure 43E indicates no melting of dodecane (i.e., all the dodecane had already melted), only lauric acid melting (as evidenced by the large carbonyl change).

Because of the importance of the previous observations (to boundary lubrication behavior), the time dependence experiment (with a 10 percent lauric acid-dodecane solution) was repeated. Figure 44 shows subtractions of pairs of the 10 percent lauric acid-dodecane solution spectra obtained in the course of this second time dependency experiment.

When the pressure was raised from ambient to 10 kbar pressure, no visual evidence for crystallization was observed. The result of subtracting the 10 kbar pressure spectrum from the ambient pressure spectrum is shown in Figure 44A. The changes observed in Figure 44A might represent either pressure effects on liquid lauric acid or they might indicate lauric acid crystallization, but the changes definitely are not due to crystallization of dodecane.

After the solution stood at 10 kbar pressure for a day, microscopic observation indicated that a small part of the solution had crystallized. The changes between zero time at 10 kbar and 1 day at 10 kbar are shown in Figure 44B. Here it can be observed that only small changes had occurred, i.e., a loss in carbonyl intensity (1700 cm^{-1}) and a gain in CH intensity (1470 cm^{-1}) with pressure.

After 3 days at 10 kbar pressure, only crystals - no liquid - could be visually observed. The spectral changes between 1 and 3 days at 10 kbar pressure are shown in Figure 44C. These changes are even smaller than seen in Figure 44B. With increasing time, the spectral changes become even smaller until they are almost unobservable as seen in Figure 44D. This figure shows the spectral changes between 18 and 23 days at 10 kbar pressure. Thus, while visual evidence indicated that crystallization started after 1 day at 10 kbar pressure and was completed after 3 days at 10 kbar pressure, the spectra indicated that lauric acid crystallized, but dodecane did not.

After 23 days at 10 kbar pressure, the pressure on the 10 percent lauric acid-dodecane solution was raised to about 11 kbar. There was slight visual evidence for further crystallization and stong spectral evidence for dodecane crystallization as shown in Figure 44E.

The purpose of this experiment was to check the reproducibility of the experiment on the 10 percent solution detailed in the preceding paragraphs. The original experiment indicated changes occurring in the solution (likely

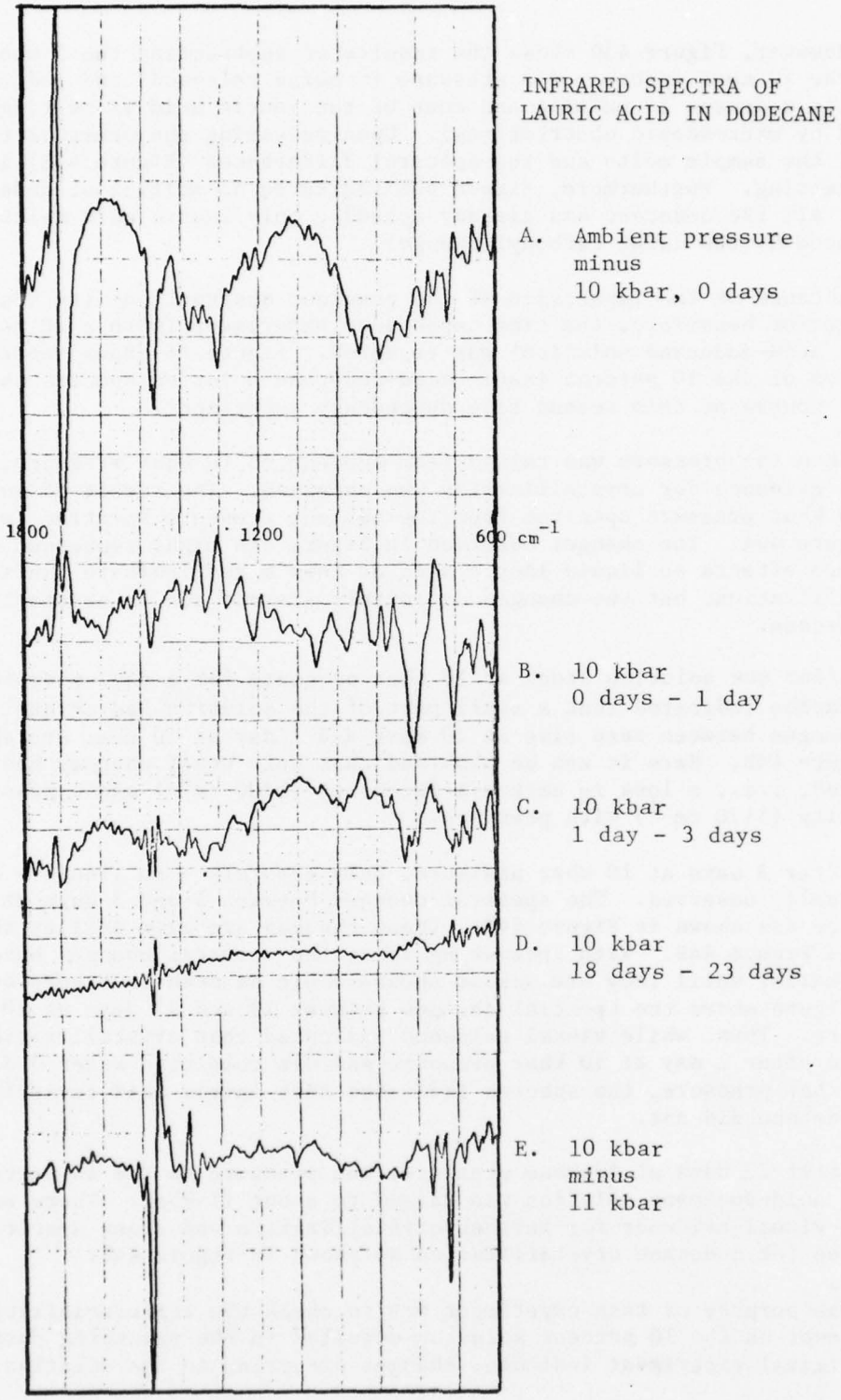


Figure 44. Subtracted Infrared Spectra of 10 Percent Lauric Acid in Dodecane

to be lauric acid aggregation) which are similar to the changes observed as lauric acid crystallized. These changes were observed with increasing time at a constant applied pressure and both lauric acid and dodecane eventually solidified at this constant pressure. In the second experiment, changes occurred with increasing time at a constant applied pressure, but eventually (by 23 days) the solution became constant and no further changes were observed (Figure 44D). However, in the current experiment, lauric acid and dodecane began to crystallize at similar, but discrete pressures.

Comparison of the first and second experiments on the 10 percent solution indicate that in this solution lauric acid and dodecane crystallize in overlapping pressure ranges. In the first experiment, it is likely that we were in the middle of this range so eventually both crystallized at the same pressure. However, in the second experiment, it is likely that the solution was near the low (or lauric acid crystallization) end of this range so a pressure increase was needed to crystallize the dodecane.

In the second experiment, when the pressure was raised to 10 kbar from ambient, changes occurred (Figure 44A) which are similar (See Figures 37C 37E and 39E) to changes previously attributed to lauric acid aggregation in solution (Figure 37C) or to lauric acid crystallization (Figures 37E and 39E). Since in the second experiment no crystallization was observed when the pressure was initially raised to 10 kbar, these spectral changes (Figure 44A) must also be attributed to lauric acid aggregation.

Figure 45 repeats (for comparison purposes) the spectrum of Figure 44E (spectral changes on raising the pressure from 10 to 11 kbar). After standing for one day at 11 kbar, the spectral evidence (Figure 45B) indicates further crystallization of dodecane, but also indicates changes in the lauric acid (note the ratio of the height of the 1710 cm^{-1} carbonyl band of lauric acid to the height of the 1470 cm^{-1} CH bands of dodecane).

During the next nine days at 11 kbar, very little change is observed (Figure 45C). Even raising the pressure to 12 kbar does not bring about much change in the solution (Figure 45D). However, after standing for 21 days at 12 kbar pressure, major changes can be observed (Figure 45E). It is important to emphasize that during the time period covered by the spectra of Figure 45, virtually no visual (microscopic) changes were observed. The spectral changes observed in Figure 45E indicate much more dodecane crystallization and more of the same type of lauric acid change as seen in Figure 45 B.

The behavior of the 10 percent solution is extremely interesting and can be summarized as follows:

(1) Both the dodecane crystallization and what is likely lauric acid crystallization are slow processes and therefore take place over a period of time at a constant applied pressure.

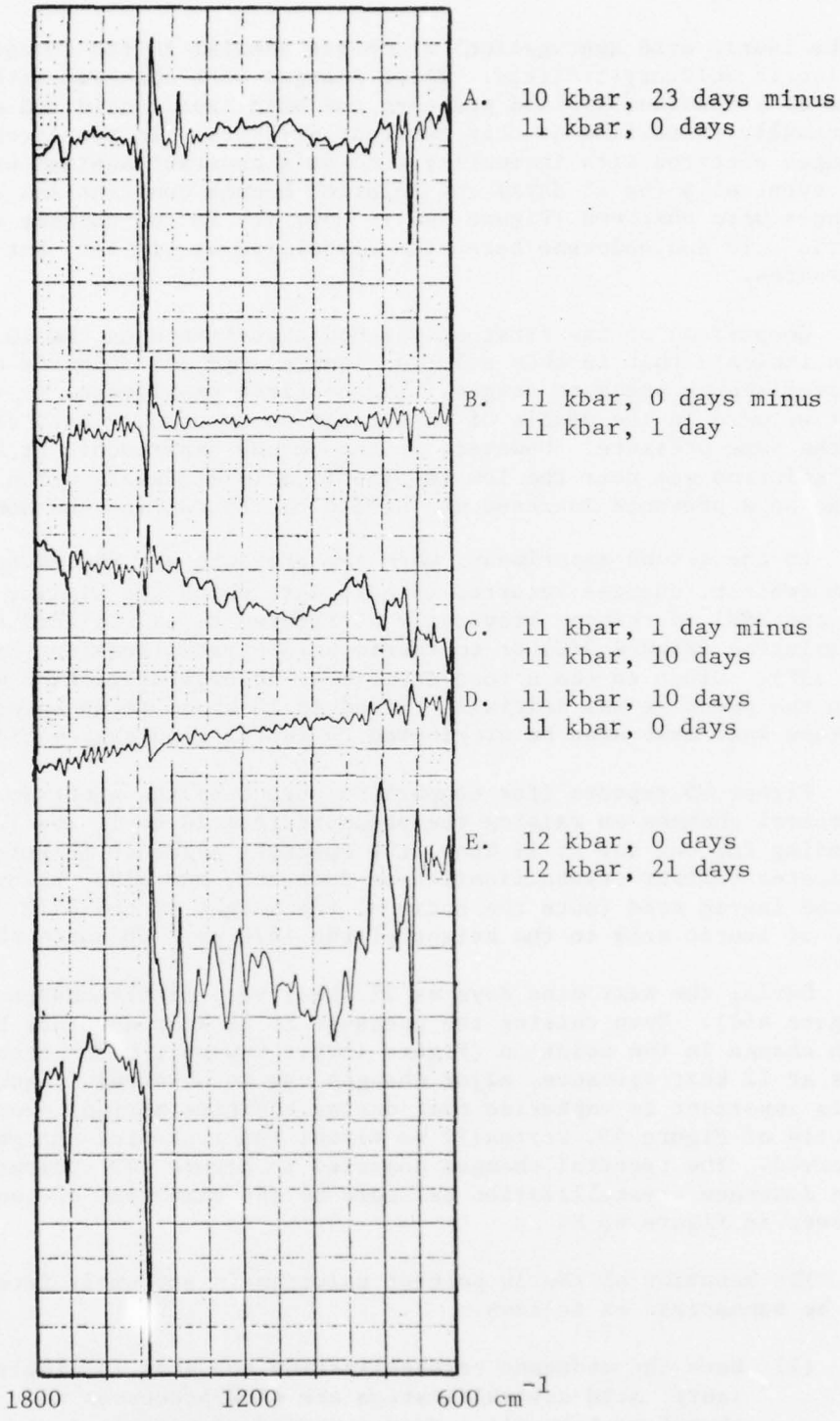


Figure 45. Subtracted Infrared Spectra of 10 Percent Lauric Acid in Dodecane

(2) At 10 kbar pressure, lauric acid begins to crystallize, but dodecane does not.

(3) At 11 kbar pressure, dodecane begins to crystallize and the lauric acid either further crystallizes or undergoes some other type of change.

(4) At 12 kbar, dodecane continues to crystallize and the lauric acid continues to change.

(5) This is an equilibrium process that covers a pressure range so raising the pressure will shift the equilibrium (towards crystallization), but will not necessarily drive the reaction to completion.

Discussion of Lauric Acid-Dodecane

Spectral Data

The subtracted spectra of Figures 4 and 5 illustrate that pressure effects on liquid dodecane can be clearly differentiated from pressure effects on solid dodecane and either of these pressure effects can be spectrally distinguished from the changes caused by pressure-induced solidifications. Thus, the infrared spectra of dodecane will reveal if the sample is all liquid, all solid, or changing from liquid to solid. When the sample is changing from liquid to solid, the spectra coupled with visual miroscopic observations can be used to tell if the sample has completely crystallized or melted.

In addition, the polarized spectra of Figures 4 and 5 show that dodecane (Figure 6) single crystals exhibit large dichroic effects and thus any pressure-induced molecular order in polycrystalline dodecane would likely be detected (Figure 7). This also illustrates that we will be able to detect small changes in molecular order as dodecane or solutions of dodecane crystallize or melt.

The fact that some molecular order exists in polycrystalline dodecane likely arises from the fact that dodecane is very slow to crystallize. Thus, even though the pressure has been raised above the solidification point (superpression), it still takes a finite period of time before thermodynamic equilibrium is established. This is illustrated by the subtracted spectra of Figure 8 where solidification or crystallization was detected after 1 hour at 10 kbars pressure (Figure 8B). However, solidification was not complete after 21 hours at 10 kbars pressure (Figure 8C) as evidenced by the fact that raising the pressure to 14 kbars (Figure 8D) indicated that solidification was still occurring.

The necessity to achieve thermodynamic equilibrium is supported by the melting data shown in Figure 9. Here (as pressure is released from 24

to <1 kbar), dodecane shows no signs of partial melting (Figures 9A, 9B, and 9C). Indeed, these spectra show only the normal (as defined in Figure 5C) effects of pressure changes on solid dodecane. It is only when the pressure is less than 1 kbar that melting can be detected (both visually and spectrally). At this point the sample rapidly and completely melts.

Since lauric acid exists as a solid at room temperature, it is more difficult to ascertain the pressure effects on liquid lauric acid than it is for dodecane (which is a liquid at room temperature), and it is also more difficult to ascertain the changes caused by pressure-induced solidification. However, Figure 12 clearly delineates the pressure effects on solid lauric acid. As previously stated in the section on lauric acid, pressure effects on solid lauric acid are large (from a spectral standpoint) compared to pressure effects on dodecane. Many IR bands of solid lauric acid show large frequency shifts with pressure changes (not seen in dodecane). All of these vibrations involve the CO or OH groups and the frequency shifts arise from the fact that pressure changes easily affect the hydrogen bond of lauric acid, i.e., an increase in pressure compresses the hydrogen bond. Thus, there are large spectral effects as the hydrogen bond of solid lauric acid is changed by pressure. On the other hand, the hydrocarbon vibrations of solid lauric acid behave much like the vibrations of the hydrocarbon chain of dodecane; that is, they exhibit an intensity change, but little or no frequency shift.

To observe the pressure effects on liquid lauric acid, it is necessary to obtain the spectra at an elevated temperature. Spectra and subtracted spectra of lauric acid (at 100 C) are shown in Figures 17 and 18, respectively. Figures 18A and 18B show that (as for liquid dodecane) pressure effects on the liquid are fewer and smaller than for the solid. For liquid lauric acid this consists mainly of a low frequency shift (with increasing pressure) of the carbonyl vibration near 1700 cm^{-1} and a small intensity increase of the 1460 and 1290 cm^{-1} vibrations.

Major changes occur as a result of pressure-induced solidification (Figure 18C), most of which have been described in the section on lauric acid and, therefore, will not be repeated here. However, one change that should be noted here is that upon solidification the carbonyl stretching frequency (near 1700 cm^{-1}) both shifts to lower frequencies and broadens considerably. Because of the low frequency shift, it is difficult to detect the broadening in the subtracted spectra (Figure 18C) between liquid and solid lauric acid. Such broadening is more easily detected by comparing the absorbance spectra of liquid (Figure 17A) and solid (Figure 17B) lauric acid. This can be seen even more readly by comparing Figures 48A and 48B in the next section which describes reactions at a metalized diamond interface. This broadening of the carbonyl vibration is important because in the lauric acid-dodecane solutions (especially the dilute solutions), the only lauric acid vibration that can be observed is the carbonyl vibration. Also, the low frequency shift upon solidification (Figure 18C) can

be confused with the low frequency shift of the carbonyl vibration when the pressure is raised on liquid lauric acid (Figure 18B). Thus in dilute solutions, the broadening of the carbonyl vibration may be the only spectral means of detecting solidification of the lauric acid.

Also of interest to note is that (at 100 C), pressure-induced solidification of lauric acid appears to occur rapidly and completely. This can be seen in Figure 18D where raising the pressure gives no evidence of further solidification. However, it should be noted that the polymorph produced by pressure at 100 C differs from the polymorph produced by melting and cooling to ambient temperature (see Figure 19). Thus, care must be taken when comparing pressure effects on various solids.

For the solutions, the spectral data can best be summarized in terms of crystallization behavior, melting behavior, and the effects of temperature. The crystallization behavior is described in Table 1, while the melting behavior is listed in Table 2 and the effects of temperature are described in Table 3.

Of interest (and not reported in the table are the effects of temperature and pressure on infrared band intensities. In general, a pressure increase brings about an increase in infrared band intensities (see, for example, Figures 19B, 21B, 28C, 30C, 32C, and 43D) unless there is a a pressure-induced solidification. Solidification brings about both increases and decreases in band intensities. A temperature increase, on the other hand, generally brings about a decrease in infrared band intensities (see Figures 30B and 32B). Therefore, a pressure increase or a temperature decrease would increase band intensities. Since these (P increase or T decrease) are conditions promoting solidification, it can be said that intensities increase as the sample becomes more like a solid.

The temperature-infrared intensity relationship is especially important in the case of the carbonyl frequency of 1 percent solutions at elevated temperatures (Figures 34 and 35). At 4 kbar pressure, the 1700 cm^{-1} carbonyl frequency decreases in intensity as the temperature is raised. At 170 C, this band has completely disappeared (to the limits of our instrumental detectability). These results indicate changes in the structure of the lauric acid (as the temperature is raised) and one possible structural change is that the high temperature is changing the hydrogen bonding from a cyclic dimer to a linear dimer or to a monomer. Some evidence for this can be seen in Figure 18C. This figure shows the difference spectrum between liquid and solid lauric acid at 100 C. As can be seen in Figure 18C, liquid lauric acid has a small band near 1745 cm^{-1} which is lost when the sample solidifies. Such a 1745 cm^{-1} band (only seen in the heated liquid) likely arises from the carbonyl vibration of a lauric acid monomer (no hydrogen bonding). The carbonyl vibration of a monomer has a smaller absorptivity than the carbonyl vibration of a dimer. Thus at 170 C, the 1 percent solution may have converted (to a large extent) to monomer, and the carbonyl vibration of the monomer would be too small to detect.

TABLE 1
CRYSTALLIZATION PRESSURES OF DODECANE AND
LAURIC ACID-DODECANE SOLUTIONS

Sample	Crystallization Pressure
Dodecane	10-14 kbar
Lauric Acid-Dodecane, 1%	10-14 kbar
Lauric Acid-Dodecane, 5%	10-14 kbar
Lauric Acid-Dodecane, 10%	
	1st Run
	Lauric Acid, 14 kbar, 20 hours
	Dodecane, 14 kbar, 40 hours
	2nd Run
	Lauric Acid, 10 kbar, 1-3 days
	Dodecane, 10-11 kbar

TABLE 2
MELTING BEHAVIOR OF DODECANE AND LAURIC ACID–DODECANE SOLUTIONS

Sample	Melting Pressure	Remarks
Dodecane	1 kbar	No partial melting.
Lauric Acid-Dodecane, 1%	2 kbar	No partial melting, no loss of order.
Lauric Acid-Dodecane, 5%	15-5 kbar	Partial melting, loss of order.
	3 kbar	Completely melted.
Lauric Acid-Dodecane, 10%	10-5 kbar	Mainly dodecane melting. No order, initially, therefore no loss of order.
	5-4 kbar	Mainly lauric acid melting. No order, initially, therefore no loss of order.

TABLE 3
CRYSTALLIZATION PRESSURES OF LAURIC ACID AND
LAURIC ACID-DODECANE SOLUTIONS AT ELEVATED TEMPERATURES

Sample	Temperature, C	Crystallization Pressure, kbar
Lauric Acid-Dodecane, 1%	23	10-14
	85	14-19
	170	No Crystallization (Up to 39 kbar)
Lauric Acid	100	14-19 (But crystallizes in different form than if melted and cooled at ambient pressure)

Another important aspect of the solution spectral data is the time behavior of the 10 percent solution (at constant applied pressure). This behavior is illustrated in Figures 40, 42, and 44. Not only do lauric acid and dodecane crystallize (or melt) separately, but the changes observed in the liquid with time (Figure 40C) indicate structuring changes in the liquid. These changes have been attributed to aggregation, or clustering of lauric acid molecules and again may be attributed to the fact that this system is very slow to reach thermodynamic equilibrium. However, the important point is that we are able to ascertain the structural changes that take place during the process of reaching thermodynamic equilibrium. Thus, we cannot only follow the melting and crystallization process, but we can follow the approach to equilibrium.

Interfacial Chemical Reactions in the Diamond Cell

The studies described in the previous sections have yielded much data on the effect of pressure on the bulk properties of fluids. Because of the inertness of diamond, no chemical reactions between solutes and substrate were observed in these experiments. This type of bulk data, though of potentially very great utility in developing models for boundary lubrication, must be supplemented by information on interfacial interactions. With some effort the diamond anvil cell can be utilized in the study of interfacial reactions. After some preliminary experiments on various methods of metalization, two diamond anvils were coated by evaporation with a layer of iron a few hundred angstroms thick. A diamond cell with these iron-coated anvils was found to transmit about 18 percent of the infrared radiation transmitted by the uncoated diamonds.

The cell was then loaded with a 10 percent solution of lauric acid in dodecane. In the process of loading, part of the iron was rubbed off of one of the diamonds so that the solution was exposed not only to iron surfaces but also to diamond. Spectra were then obtained at ambient pressure and 8 kbar. The weak bands near 895 cm^{-1} and 1118 cm^{-1} in Figure 46A indicate that small amounts of material had crystallized. Also, the breadth of the carbonyl (1710 cm^{-1}) vibration of lauric acid indicates the presence of crystalline lauric acid, indicating that the crystalline material responsible for the weak bands near 895 cm^{-1} and 1118 cm^{-1} is lauric acid. At 8 kbar (Figure 46B), the 895 cm^{-1} and 1118 cm^{-1} are more intense, indicating that some dodecane had crystallized. Figure 46C shows that no further changes occurred after the specimen was kept at 8 kbar for 16 hours.

The changes seen in Figure 46 can be more easily followed in Figure 47 which shows various difference spectra. These spectra indicate the following:

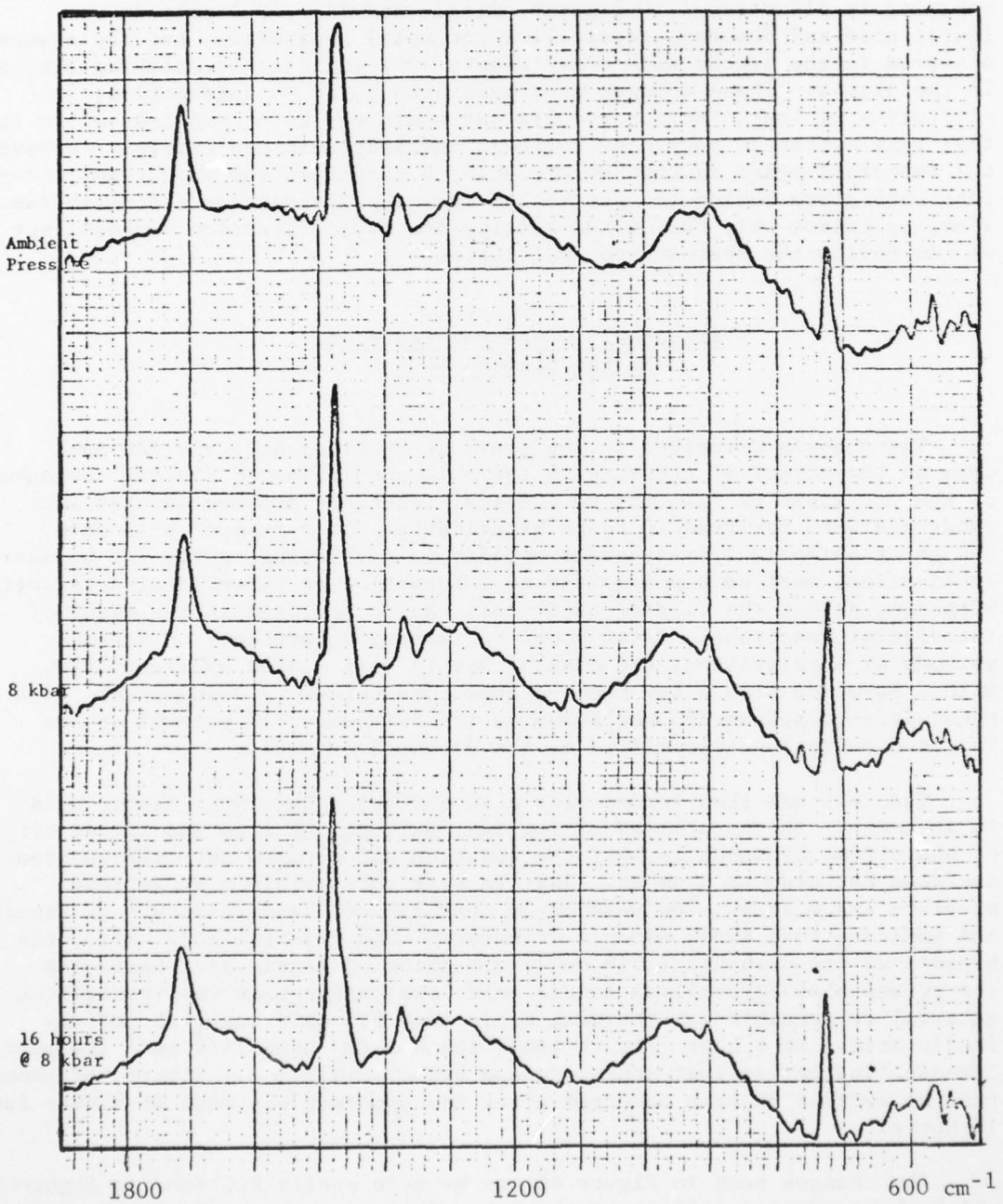


Figure 46. Infrared Spectra of a 10 Percent Lauric Acid-Dodecane Solution (Fe-Coated Diamond Windows)

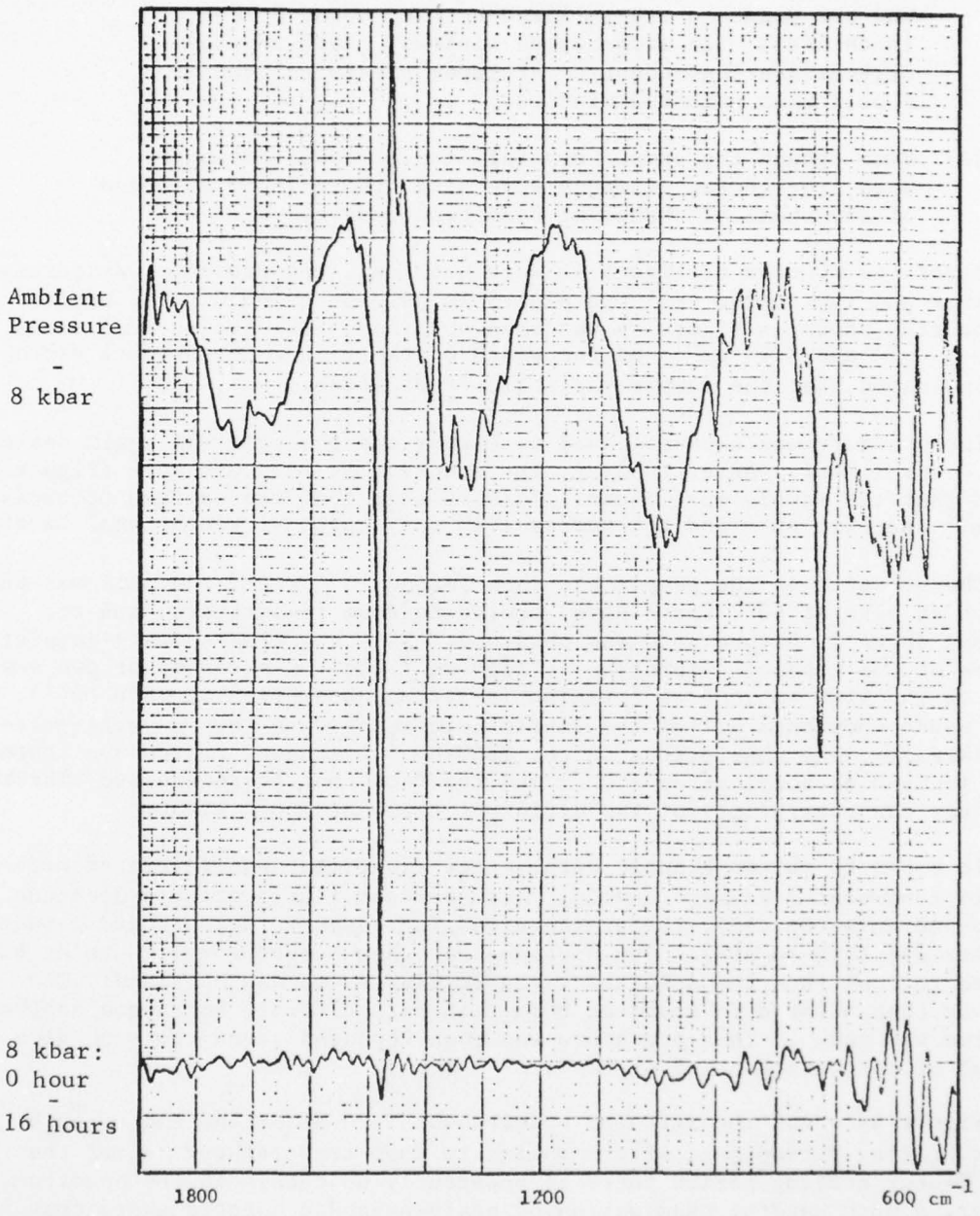


Figure 47. Subtracted Infrared Spectra of 10 Percent Lauric Acid-Dodecane Solution (Fe-Coated Diamond Windows)

(1) The lauric acid crystallized near ambient pressure and the dodecane crystallized between 0 and 8 kbar in the cell with iron-coated windows. Both of these crystallizations occurred at lower pressures than in a cell with uncoated windows.

(2) Even though the sample crystallized at lower pressures when iron-coated diamonds were used, there is no evidence of any chemical change at room temperature.

After the spectra of Figure 46 were obtained, the pressure was released to 6 kbar and the entire cell was placed in an oven at 60 C for 1 hour. The spectrum shown in Figure 48 was then obtained. The presence of bands near 895 cm^{-1} and 1118 cm^{-1} and the width of the 1710 cm^{-1} carbonyl vibration indicated that the sample was still crystalline.

The pressure was then released to 1 kbar and the cell was again heated at 60 C for 1 hour. After cooling, the spectrum at this pressure (Figure 48B) showed that the sample was liquid. This is seen from the absence of bands at 895 cm^{-1} and 1118 cm^{-1} and the narrow 1710 cm^{-1} carbonyl vibrational band.

The pressure on the sample was then raised to 6 kbar, the cell was put back in an oven at 60 C for 4 days, cooled to room temperature, and the spectrum shown in Figure 48 C was obtained. This spectrum shows a complete absence of the carbonyl vibration at 1710 cm^{-1} and the presence of two new bands in the 1500 to 1600 cm^{-1} region (a strong absorption at 1550 cm^{-1}). These bands show that <u>all</u> of the lauric acid reacted to form a metal salt-iron laurate. The absorptions in the 1500 cm^{-1} frequency region are those of an ionized carboxyl group (COO^-) and the fact that there are two vibrations indicates the possibility of two different types of COO^{-1} group.

In order to obtain kinetic data, a new experiment was initiated with freshly iron-coated diamond anvils. A 10 percent lauric acid in dodecane was loaded into the cell, the pressure was increased to 6 kbar, and a spectrum was obtained (Figure 49A). The specimen was then heated for 2 hours at 60 C, allowed to cool, and the spectrum given in Figure 49B was obtained. The cell was then allowed to stand at room temperature for 16 hours and another spectrum was taken. This procedure was then repeated seven times to give a total of 14 hours heating at 60 C.

Figure 49 shows the infrared spectra obtained after the end of each 2-hour heating period just after cooling to room temperature. After the first 2-hour heating period there is apparently no change in the spectrum. However, a more careful examination of scale-expanded spectra shows that a very small infrared band arising from the COO^{-1} vibration of iron laurate can be seen near 1550 cm^{-1}. This absorption can be seen more clearly in Figure 49C (4 hours heating at 60 C).

The slow growth of the 1550 cm^{-1} band and the disappearance of the acid carbonyl vibration at 1710 cm^{-1} can be followed in Figures 49D through 49G.

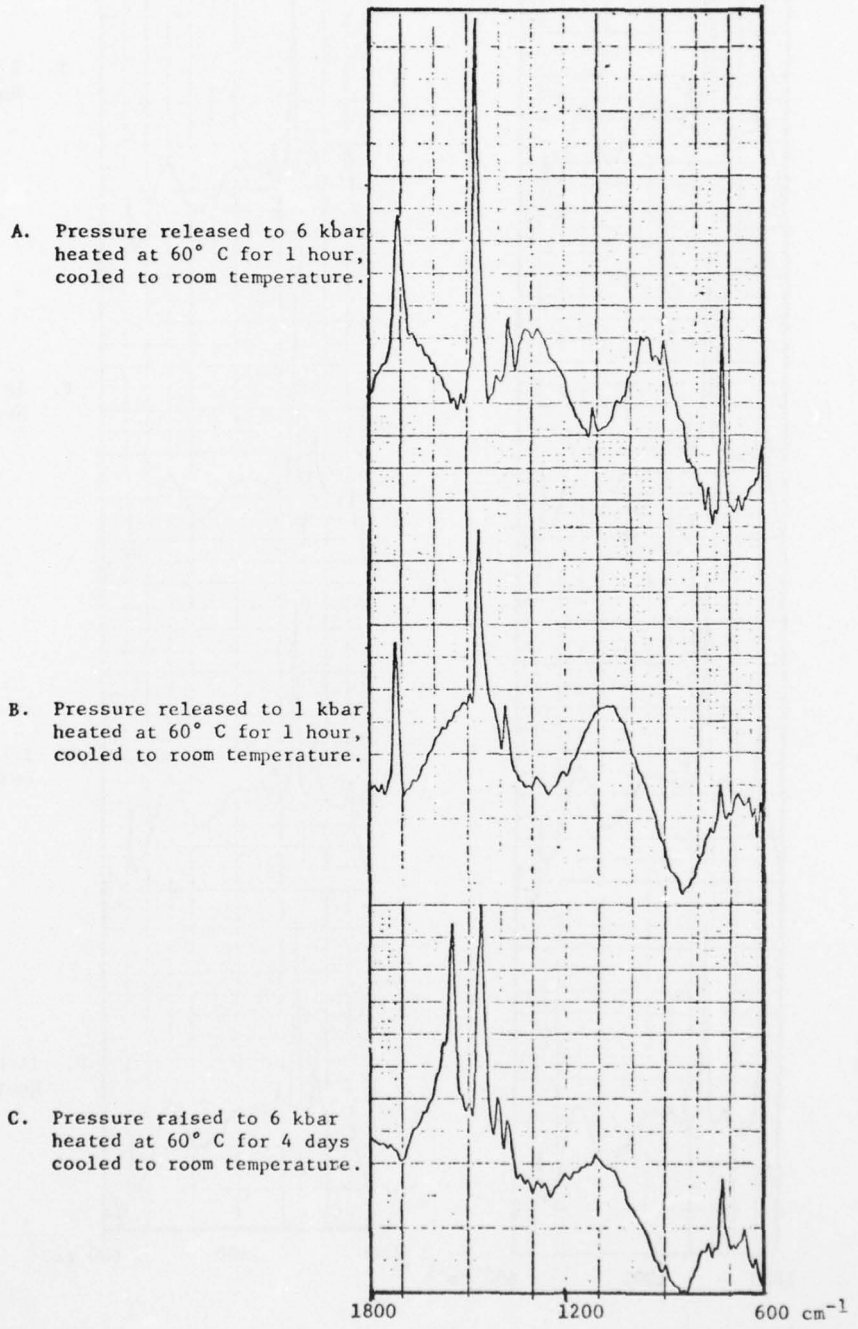


Figure 48. Infrared Spectra of a 10 Percent Lauric Acid-Dodecane Solution (Fe-Coated Diamond Windows)

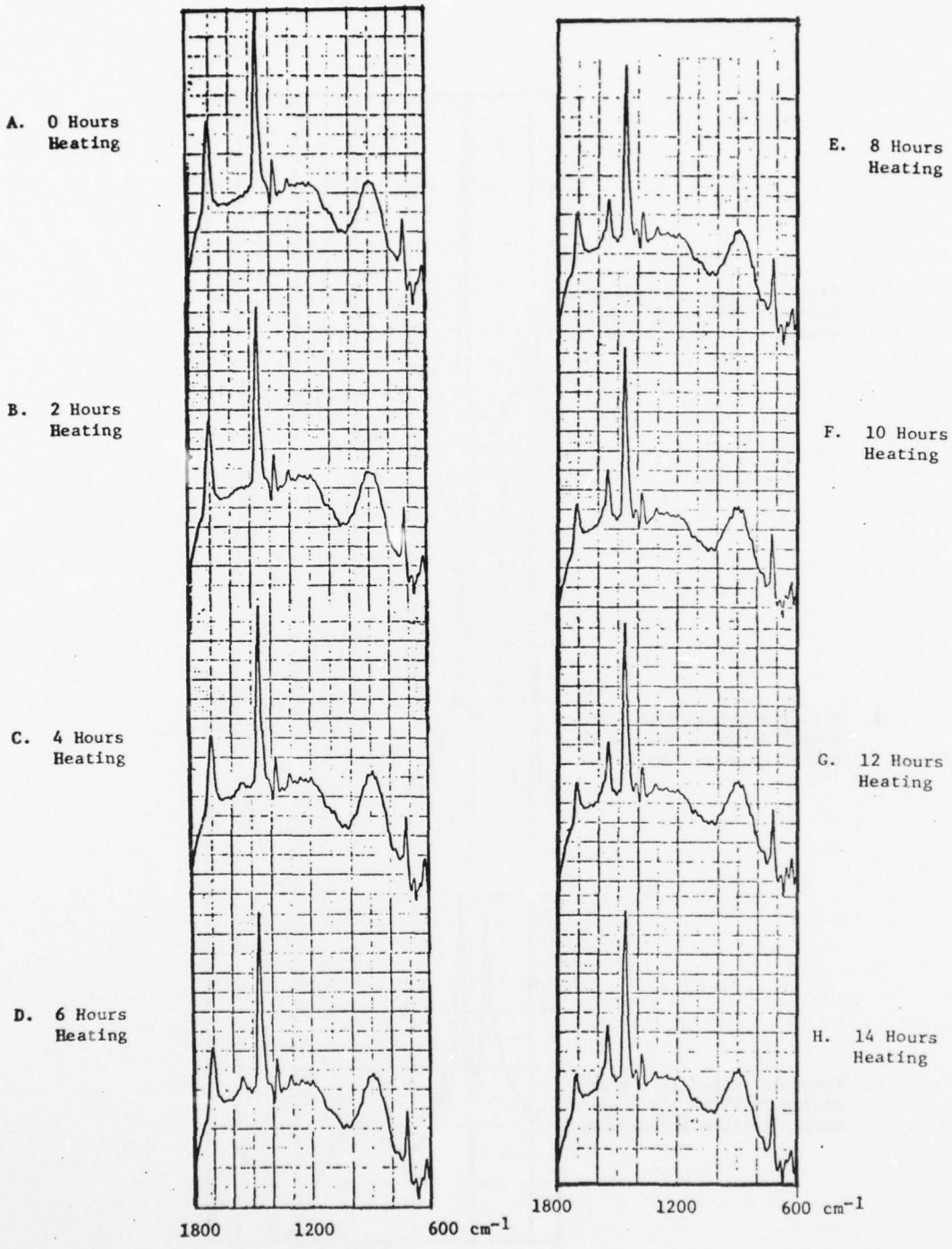


Figure 49. Infrared Spectra of a 10 Percent Lauric-Acid Dodecane Solution at 6 kbar Pressure and After Heating for Various Periods at 60 C (Fe-Coated Windows)

After 14 hours at 60 C, the reaction is about 60 percent complete (as judged by comparison of the 1710 cm^{-1} band intensity with the original intensity of this band seen in Figure 49A).

The rate of the reaction can be more easily observed in Figure 50 which is a plot of absorbance of the 1710 cm^{-1} lauric acid carbonyl band versus time. From this plot it can be seen that there is a finite period of time (2 hours) before any reaction can be detected. The reaction proceeds at a fairly uniform rate between 2 hours and 10 hours heating at 60 C and appears to slow down after 10 hours.

The spectra obtained after the cell stood at room temperature for 16 hours show little difference between the corresponding spectra taken shortly after each heating period. A very small loss in the intensity of the acid carbonyl band (1710 cm^{-1}) and a very small gain in the intensity of the COO^- (1550 cm^{-1}) band can be observed, indicating that the reaction is proceeding at room temperature but at a much slower rate than at 60 C.

A control experiment, in which a 10 percent lauric acid in dodecane solution was heated for 4 days at 60 C, showed no changes in the intensity of the carbonyl band at 1710 cm^{-1} or formation of a COO^- band at 1550 cm^{-1} (Figure 51). This experiment demonstrates that the changes in these two bands observed in the iron-coated anvil experiments are really caused by reaction with the iron rather than by heating or reaction with the platinum gasket.

Preliminary Study of a Diester (E-105) and Tricresyl Phosphate

Spectra were obtained in a diamond window high-pressure cell using a platinum (Pt) gasket (~2 mils thick) to contain the liquid samples. As can be seen from the spectra (Figures 52-54), this Pt gasket was too thick and very intense spectra were obtained. While frequency shifts can be observed even with the thick gaskets, spectral subtraction is not as reliable as when less intense bands are used.

Figure 52 shows infrared spectra of E-105 at ambient pressure (Figure 52 and 52B) at ~20 kbar (Figure 52b). Figure 52C shows the resultant of subtracting the spectrum of Figure 52B from that of Figure 52A. This subtraction spectrum shows several bands pointing up (1740, 1180, and 1140 cm^{-1}m CO vibrations), and two bands pointing down (1460 and 1380 cm^{-1}, CH vibrations). No dispersion curves (part of the band pointing up and part of the band pointing down, see Figure 53) are evident. The lack of dispersion curves indicates that there are no frequency shifts with increasing pressure. Yet the bands pointing upwards and down indicate intensity changes with the CH vibrations becoming less intense with increasing pressure and the CO vibrations becoming more intense with increasing pressure.

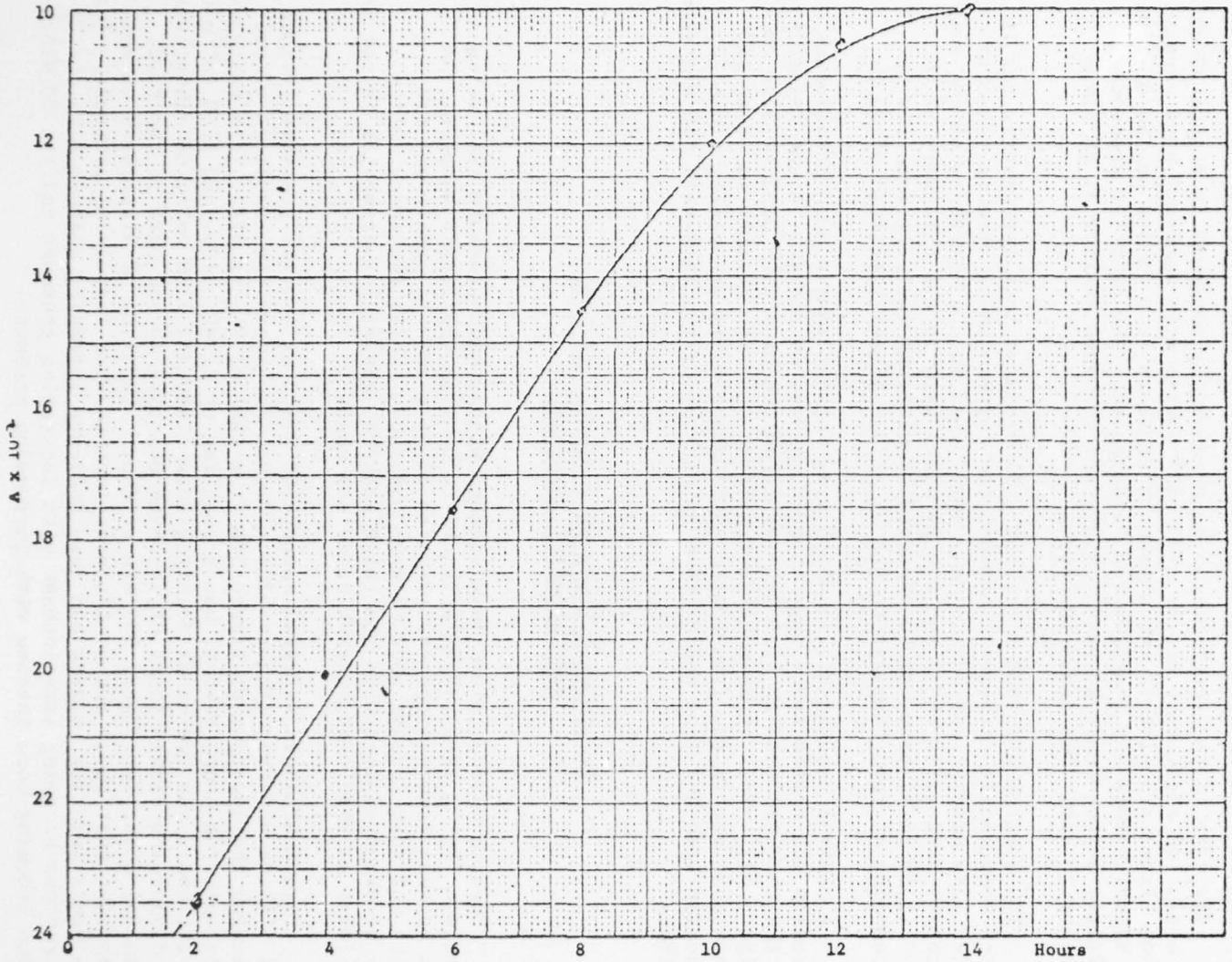


Figure 50. Absorbance of 1710 cm^{-1} Carbonyl Vibration as a Function of Heating Time at 60 C

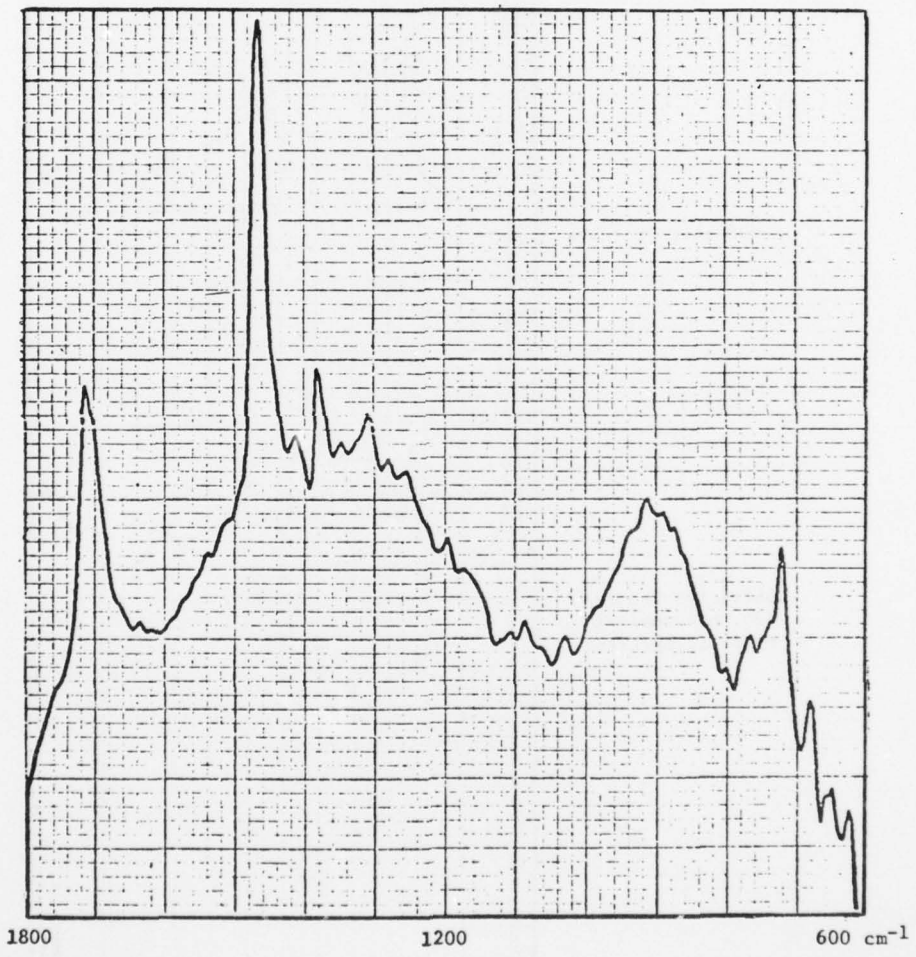


Figure 51. Infrared Spectrum of a 10 Percent Lauric Acid-Dodecane Solution at 6-kbar Pressure and After Heating 4 Days at 60 C

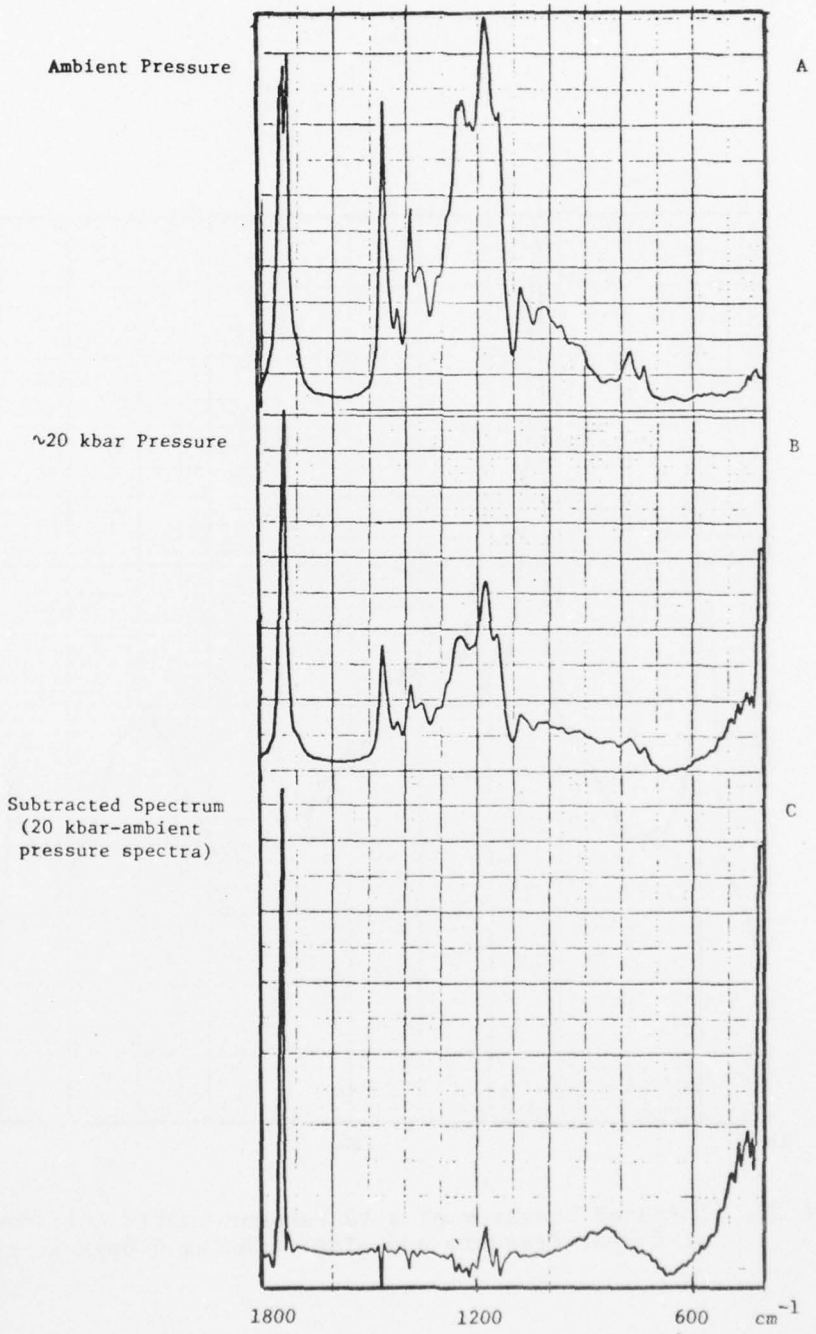


Figure 52. Infrared Spectra of E-105

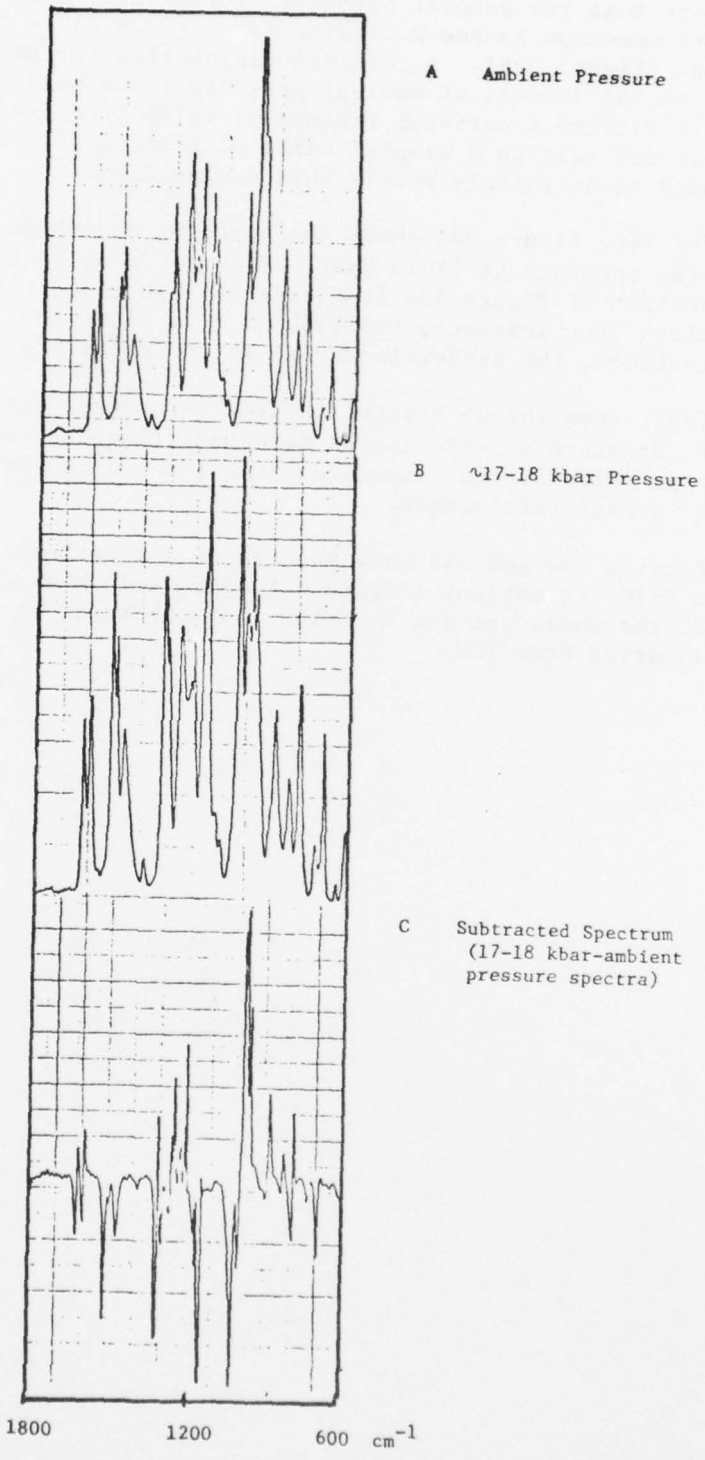


Figure 53. Infrared Spectra of TCP

Note that the doublet carbonyl vibration (around 1740 cm^{-1}) in the ambien pressure spectrum became a singlet (at 1740 cm^{-1}) in the high pressure spectrum (Figure 52B). A possible explanation for this behavior is a mixture of rotational isomers at ambient pressure (each rotational isomer having a slightly different carbonyl frequency) which pressure forces into one or the other isomer (giving a singlet carbonyl frequency). Further experimentation is needed to definitely verify this explanation.

For TCP, Figure 53A shows the spectrum at ambient pressure and Figure 53B gives the spectrum at 17-18 kbar. Figure 53C shows the result of subtracting the spectrum of Figure 53A from that of Figure 53B. Here both intensity variations (for instance, the 1460 cm^{-1} CH vibration) and frequency shifts (for instance, the dispersion curve at 800 cm^{-1}) are observed.

Thus, even though crystallization was not observed in either E-105 or in TCP, pressure effects can be detected (frequency shifts and/or intensity changes). With further experimentation, these can be related to pressure-induced structural changes.

Figures 51A and 54B show spectra of a 1 percent (by volume) solution of TCP in E-105 at ambient (Figure 54A) and 14-15 kbar (Figure 52B) pressure. Most of the bands are due to E-105, but the bands at 500 and 980 cm^{-1} clearly arise from TCP.

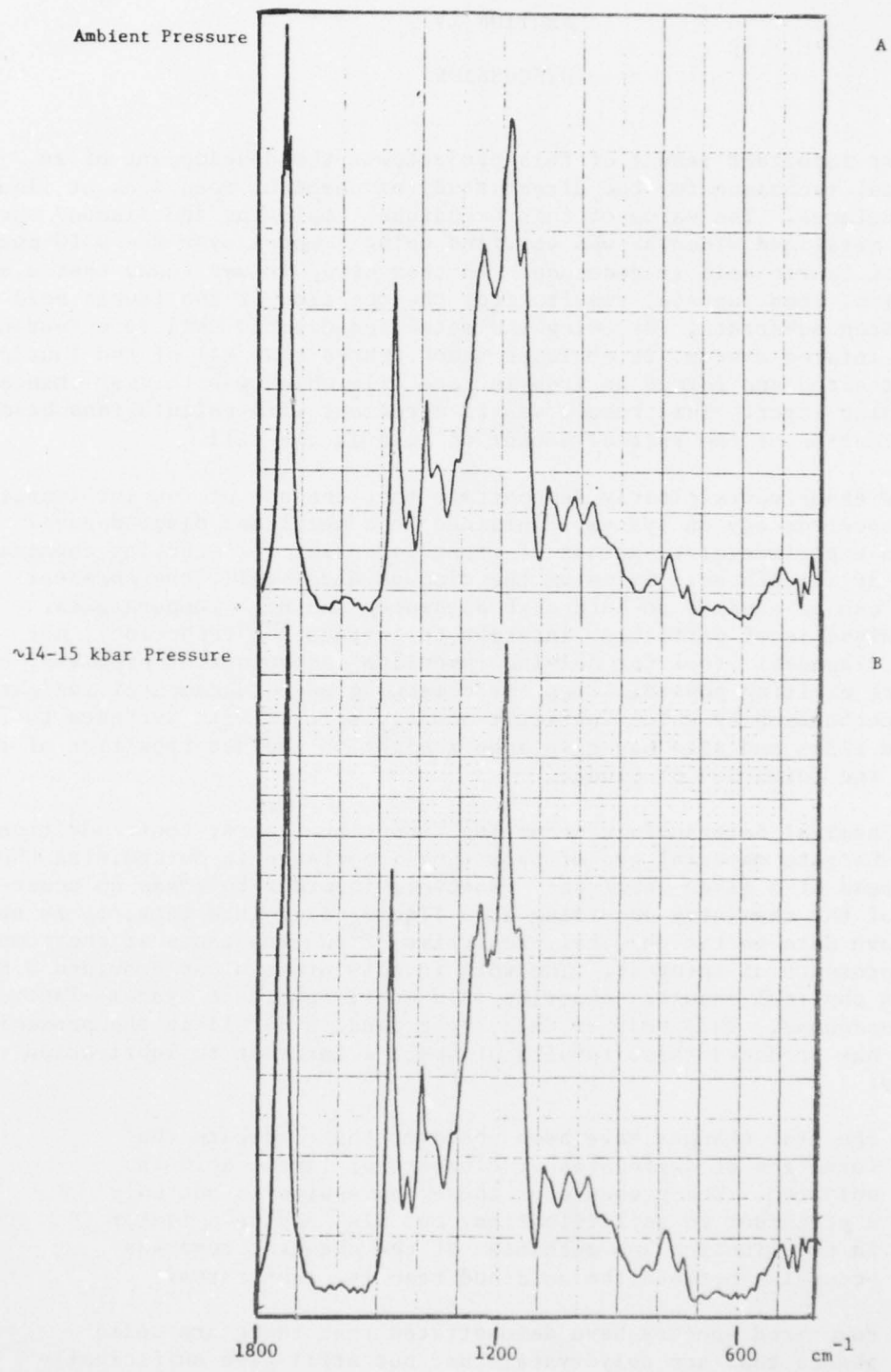
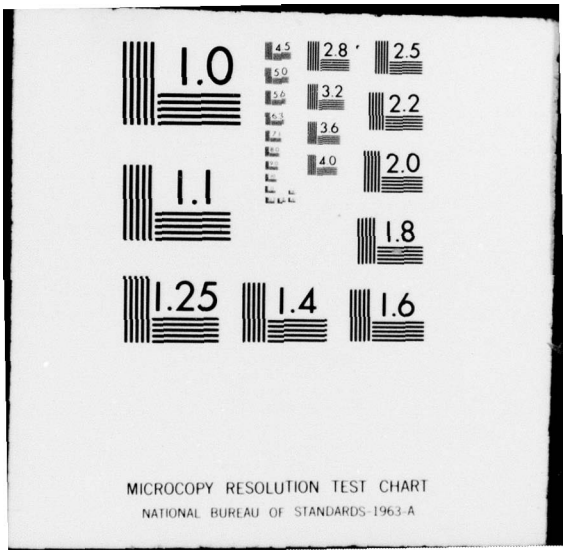


Figure 54. Infrared Spectra of a One Percent Solution of TCP in E-105

AD-A067 359 BATTELLE COLUMBUS LABS OHIO F/G 11/8
SOLIDIFICATION OF BOUNDARY LUBRICANT FILMS.(U)
DEC 78 E J DRAUGLIS, R J JAKOBSEN F33615-77-C-2026
UNCLASSIFIED AFAPL-TR-78-111 NL

2 OF 2
AD
A067359

END
DATE
FILMED
6-79
DDC


1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0
5.6
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

SECTION IV

DISCUSSION

A most important result of this project was the development of an experimental technique for the direct study of chemical reactions at liquid-solid interfaces. The value of this technique, employing the diamond anvil cell with metalized windows, was verified using a model system - a 10 percent solution of lauric acid in dodecane. In this study it was found that a surface species, iron laurate, results from the reaction of the lauric acid with the iron substrate. By using the metalized diamond cell in a Fourier Transform infared system, it could be demonstrated that all of the lauric acid had reacted and formed an iron laurate film which was thicker than a monomolecular layer. This result was in agreement with calculations based on an estimation of the initial amount of acid in the cell.

These experiments clearly demonstrate that the use of Fourier Transform infrared spectroscopy on systems contained in a metalized diamond anvil cell is an experimental technique of great potential for studying chemical reactions at interfaces. By using the diamond anvil cell, the chemical reactions can be studied at both high pressures and high temperatures. This technique is of particular interest to lubrication technology, not only as a diagnostic tool for solving immediate technological problems, but also offers exciting possibilities for obtaining more fundamental insights into the mechanisms by which lubricant additives react with surfaces to form protective films and also may give some insight on the decomposition of lubricants and the formation of sludge.

The chemical interactions occurring among lubricants, their additions, and the substrate material are of promising importance in determining the effectiveness of a given lubricant. However, in order to grasp an understanding of the chemistry occurring at a liquid-solid interface, it is necessary to have data on the physical properties of the reactants at the temperature and pressure of interest. The work in this program has provided a body of data on physical changes occurring in a model lubricant system--lauric acid and dodecane. This body of data, described in detail in the proceding sections, has produced three results of special interest to lubrication technology:

(1) Spectral changes have been observed that indicate the formation of aggregates or clusters of lauric acid in solution. The presence of these aggregates is not only a precursor to solidification, but also may be a factor in the kinetics and mechanism of the chemical reaction occurring between the acid and reactive substrates.

(2) Polarized spectra have demonstrated that there are solid phases that are polycrystalline, but still give sufficiently high dichroic ratios to indicate a significant degree of long-range order.

(3) Superpression effects have been detected in all of the straight chain systems studied. That is, the systems tended to remain liquid up to pressures much higher than indicated by the melting behavior. For example, dodecane remained liquid until pressures above 10 kbar were attained. Yet upon pressure release it was found that melting did not occur until the pressure was decreased to about 1 kbar.

Late in this program it was found that Dr. J. M. Schnur and his associates at the U.S. Naval Research Laboratory were also performing experiments on straight chain alkanes hydrocarbons in a diamond cell. In these studies, Raman spectroscopy is being used to study the conformation of the alkane molecules. Much work has been performed on the conformational analysis of such molecules.[11,12] Because of the low barrier to rotation about a C-C bond, such molecules are not rigid (hard rods) in the liquid state, but contain one or more kinks. However, since these molecules are fully extended kinklers in the solid state, it was generally believed that as pressure on a liquid straight-chain alkane is increased until solidification occurs, there would be a straightening out of the molecules. The work of Schnur indicates that this is not true. They found that as the pressure is increased the fraction of kinked molecules rises sharply.[13] Unfortunately, these workers have worked only with pure solvents rather than solutions. However, their work has potential application to the understanding of the formation of the aggregates observed in the present program. It is also of interest because in later work they have obtained evidence for a liquid crystalline phase in normal $CH_3(CH_2)_{38}CH_3$[14]. This is additional evidence for the model proposed some time ago by workers at Battelle's Columbus Laboratories which explained the observed properties of squeeze films formed from a wide variety of hydrocarbon solvents. The essential feature of this model is that straight-chain alkane solvents can posses smectic liquid crystalline order. The work of Schnur is the first independent corroboration of this hypothesis evidence in support of which is given in Reference 1.

---

(11) Snyder, R. G., "Vibrational Study of the Chemical Conformation of the Liquid n-Paraffins and Molten Polyethylene", J. Chem. Phys., 47, 1316 (1967).

(12) Bartill, L. S., and Kohl, D. A., "Structure and Rotational Isomerization of Free Hydrocarbon Chains", J. Chem. Phys., 39, 3097 (1963).

(13) Schoen, P. E., Priest, R. G., Sheridan, J. P., and Schnur, J. M., "Pressure-Induced Changes in Molecular Conformation in Liquid Alkanes", Nature, 270, 412 (1977).

(14) Schoen, P. E., Priest, R. G., Sheridan, J. P., and Schnur, J. M., Publication expected in 1979.

SECTION V

BIBLIOGRAPHY

1. Allen, C. M., Drauglis, E., Glaeser, W. A., Alexander, C. A., and Jakobsen, R. J., "Aircraft Propulsion Lubricating Film Additives: Boundary Surface Films" Report to Air Force Aero Propulsion Laboratory AFAPL-TR-73-121, Volume III, June, 1976.

2. Allen, C. M. and Drauglis, E. "Boundary Lubrication: Monolayer or Multilayer" Wear 14, 363 (1969).

3. Ferraro, J. R., "High Pressure Vibrational Spectroscopy" in Spectroscopy in Inorganic Chemistry, Vol. II, P. 57, C.N.R. Rao and J. R. Ferraro, Eds., Academic Press, New York 1971.

4. Melveger, A. J., "High Pressure Vibrational Spectroscopy" in Vibrational Spectra and Structure, Vol. 1, J. R. Durig, Ed., P. 51, Marcel Dekker, Inc., New York, 1972

5. Adams, D. M., Payne, S. J., and Martin, K., "The Fluorescence of Diamond and Raman Spectroscopy at High Pressures Using a New Design of Diamond Anvil Cell", Applied Spectroscopy, 27, 377 (1973).

6. Lauer, J. L., "High Pressure Infrared Interferometry" in Fourier Transform Infrared Spectroscopy, J. R. Ferraro and L. J. Basil, Eds., P. 169, Academic Press, New York, 1978.

7. Ferraro, J. R. and Basile, L. J., "Spectroscopy at High Pressures-- Status Report and Update of Instrumental Techniques", Applied Spectroscscopy 28, 505 (1974).

8. Adams, D. M., and Payne, S. J., "Vibrational Spectroscopy of Solids at High Pressures", Annual Reports on Progress of Chemistry 69A, 3 (1972).

9. Griffiths, P., Chemical Infrared Fourier Transform Spectroscopy, John Wiley & Sons, New York, 1975.

10. Nelson, R. R., Webb, W., and Dixon, J. A., "First-Order Phase Transitions of Six Normal Paraffins at Elevated Pressures", J. Chem. Phys., 33, 1756 (1960).

11. Snyder, R. G., "Vibrational Study of the Chemical Conformation of the Liquid n-Paraffins and Molten Polyethylene", J. Chem. Phys., 47, 1316 (1967).

12. Bartill, L. S., and Kohl, D. A., "Structure and Rotational Isomerization of Free Hydrocarbon Chains", J. Chem. Phys., 39, 3097 (1963).

Distribution List

Aerospace Corporation
Attn: Library Acquisition Group
PO Box 92957
Los Angeles, California 90009

Airesearch Mfg. Co. of Arizona
Chief, Matls. Engineering Dept. 93-03M
PO Box 5217
402 S. 36th Street
Phoenix, Arizona 85010

Atlantic Richfield Company
Harvey Technical Center
Attn: Tom J. Clough
400 E. Sibley Blvd.
Harvey, Illinois 60426

Avco-Everett Research Laboratory
Technical Library
Attn: Mrs. Lorraine Nazzaro
2385 Revere Beach Parkway
Everett, Massachusetts 02149

Avco Lycoming Division
Attn: Division Library
550 South Main Street
Stratford, Connecticut 06497

The Barden Corporation
Attn: Harold R. Berglund
Dept. 76
200 Park Avenue
Danbury, Connecticut 06810

Battelle's Columbus Laboratories
Attn: D. K. Snediker
505 King Avenue
Columbus, Ohio 43201

Battelle's Columbus Laboratories
Attn: Mr. Jerry Kannel
Engineering Systems Department
505 King Avenue
Columbus, Ohio 43201

Battelle Memorial Institute
Attn: Reports Library
505 King Avenue
Columbus, Ohio 43201

Bell Aerospace Company
Technical Library
Attn: Mrs. Eunice P. Hazelton
PO Box 1
Buffalo, New York 14240

The Bendix Corporation
Navigation & Control Division
Attn: Mrs. Lydia M. Farrell
Dept. 7849
Teterboro, New Jersey 07608

The Bendix Corporation
Research Laboratories
Attn: Dr. W. M. Spurgeon
20008 Civic Center Drive
Southfield, Michigan 48076

The Bendix Corporation
Engineering Library, Dept. 8310
Attn: S. A. Park
211 Seward Avenue
Utica, New York 13503

Boeing Computer Services
Attn: John Laakso
Mailstop 3N-18
PO Box 24346
Seattle, Washington 98124

The Boeing Company
Attn: Library - Wichita Division
Wichita, Kansas 67210

The Boeing Company
Aerospace Group
Attn: Mr. Jan W. Vanwyk - 2-5540
Box 3999
Seattle, Washington 98124

The Boeing Company
Vertol Division
Attn: A. J. Lemanski
Boeing Center, P.O. Box 16858
Philadelphia, Pennsylvania 19142

Borg-Warner Corporation
Research Center
Attn: Research Library
Wolf & Algonquin Roads
Des Plaines, Illinois 60018

California Institute of Tech.
Jet Propulsion Laboratory
Opers Group, Acquisitions 111-113
4800 Oak Grove Drive
Pasadena, California 91103

Carpenter Technology
Attn: Thoni Philip
Carpenter Steel Division
Reading, Pennsylvania 19603

Catholic University of America
Attn: Prof. T. Litovitz
Dept. of Physics
Vitreous State Laboratory
Washington, D.C. 20017

CBS Laboratories
Attn: R. J. Roper
227 High Ridge Road
Stamford, Connecticut 06905

Chevron Research Company
Attn: Mr. Neal W. Furby
PO Box 1627
Richmond, California 94804

Ciba-Geigy Corporation
Polymer Additives Department
Attn: Philip J. Pare
Saw Mill River Road
Arosley, New York 10502

Curtiss-Wright Corporation
Wood-Ridge Facility
1 Passaic Street
Woodridge, New Jersey 07075

Detroit Diesel Allison
Attn: Library S5
PO Box 894
Indianapolis, Indiana 46206

Detroit Diesel Allison
Division of GM
Attn: Library (W. H. Richardson)
PO Box 894
Indianapolis, Indiana 46206

The Dow Corning Corporation
Attn: Library (22)
592 Saginaw Road
Midland, Michigan 48640

Eastman Kodak Company
Engineering - B-23
Attn: Mr. J. W. John
Kodak Park
Rochester, New York 14650

E. I. DuPont de Nemours & Company
Petroleum Laboratory
Attn: Wilfred E. Bettoney
Wilmington, Delaware 19898

Emery Industries, Inc.
Attn: Bruce Beimesch
4900 Este Avenue
Cincinnati, Ohio 45232

Engineering Societies Library
Acquisitions Department
345 East 47th Street
New York, New York 10017

Exxon Research & Engineering Company
Products Research Division
Attn: Dr. Stephen J. Metro/Aviations
Lubricants
PO Box 51
Linden, New Jersey 07036

Exxon Company, USA
Attn: E. S. Swanson, Jr.
PO Box 389
Florham Park, New Jersey 07932

The Fafnir Bearing Company
Attn: H. B. Vandorn
New Britain, Connecticut 06050

FAG Bearing Corporation
Attn: Pat E. Nicolich
Hamilton Avenue
Stamford, Connecticut 06904

Fairchild Industries, Inc.
Fairchild Republic Div.
Attn: Henry W. Kleindienst
Conklin Street
Farmingdale, New York 11735

Federal-Mogul Corporation
Attn: Charles W. Williams
3980 Research Pk. Dr.
Ann Arbor, Michigan 48104

Ford Motor Company
Scientific Research Labs.
Attn: Mrs. L. B. Phillips
PO Box 2053
Dearborn, Michigan 48121

The Franklin Institute Research Labs.
Attn: Mr. John Rumbarger
20th & The Parkway
Philadelphia, Pennsylvania 19006

The Franklin Institute Research Labs.
Attn: Mr. Wilbur Shapiro
20th & The Parkway
Philadelphia, Pennsylvania 19006

The Franklin Institute Research Labs.
Mechanical Engineering Laboratory
Attn: Wilbur Shapiro
20th and Race Streets
Philadelphia, Pennsylvania 19103

The Garrett Corporation
Airesearch Mfg. Div. of Arizona
Attn: Librarian
PO Box 5217
Phoenix, Arizona 85010

General Dynamics
Convair Aerospace Div.
Attn: U. J. Sweeney, Ch. Librarian
PO Box 80986
San Diego, California 92112

General Dynamics
Convair Aerospace Div.
Attn: Technical Library
PO Box 748
Fort Worth, Texas 76101

General Electric Company
Attn: Dr. C. Y. Chow
Gas Turbine Department 53-338
1 River Road
Schenectady, New York 12345

General Electric Company
Aircraft Engine GP/Engineering Section
Attn: TIC 24001
1000 Western Avenue
Lynn, Massachusetts 01910

General Electric Company
Aircraft Engine GP
Materials & Processing Technology Lab.
Attn: E. N. Bamberger/M-82
Cincinnati, Ohio 45215

General Electric Company
Aircraft Engine Group
Attn: D. B. Hester
Mail Stop M-82
Cincinnati, Ohio 45215

General Motors Corporation
Research Laboratories
Attn: Mr. Fred Rounds
12 Mile and Mound Roads
Warren, Michigan 48090

General Motors Research Labs.
Mechanical Research Dept.
Attn: Roland Maki
12 Mile and Mound Roads
Warren, Michigan 48090

Georgia Institute of Technology
Attn: Mr. W. O. Winer
Department of Mech. Engineering
Atlanta, Georgia 30332

W. R. Grace & Company
Hatco Chemical Division
Attn: Harry F. Reid
King George Post Road
Fords, New Jersey 08863

Gulf Research & Development Company
Petroleum Products Department
Attn: R. P. Foster
PO Drawer 2038
Pittsburgh, Pennsylvania 15230

Hercules, Inc.
Synthetics Department
Attn: Paul Page
Wilmington, Delaware 19899

Hughes Aircraft Company
Attn: B. W. Campbell
Bldg. 6, MS E110
Centinela and Teale Street
Culver City, California 90034

IIT Research Institute
Attn: Document Library
10 West 35th Street
Chicago, Illinois 60616

Jet Propulsion Laboratory
California Institute of Technology
Attn: Library Oper Gr (Acquis.)
4800 Oak Grove Drive
Pasadena, California 91103

Lear Siegler, Inc.
Engineering Library
Attn: R. W. Voss
17600 Broadway Avenue
Maple Heights, Ohio 44022

Lockheed-California Company
Central Library
Attn: Acquisition Librarian
2555 North Hollywood Way
Burbank, California 91503

LTV Aerospace Corporation
Vought Aeronautics Company
Attn: Thomas P. McGinty
PO Box 5907
Dallas, Texas 75222

Marlin-Rockwell Div. Trw.
Attn: Mr. Arthur S. Irwin
402 Chandler Street
Jamestown, New York 14701

Marlin Rockwell Div. of TRW, Inc.
Research Dept.
Attn: Harold E. Munson
402 Chandler Street
Jamestown, New York 14701

Massachusetts Inst. of Technology
Mechanical Engineering Dept.
Attn: Prof. B. G. Rightmire
77 Massachusetts Avenue
Cambridge, Massachusetts 02139

Massachusetts Inst. of Technology
Metallurgy & Materials Science
Attn: Prof. B. L. Averbach
77 Massachusetts Ave.
Cambridge, Massachusetts 02139

McDonnell Aircraft Company
Attn: Mr. J. M. Sinnett
MS 331
PO Box 516
St. Louis, Missouri 63166

Mechanical Technology, Inc.{
Attn: J. Walwit
968 Albany-Shaker Road
Latham, New York 12110

Mechanical Technology, Inc.
Attn: Leo Winn
968 Albany-Shaker Road
Latham, New York 12110

Mechanical Technology, Inc.
Tribology Center
Attn: E. B. Arwas
968 Albany-Shaker Road
Latham, New York 12110

Midwest Research Institute
Attn: Vern Hopkins
425 Volker Blvd.
Kansas City, Missouri 64110

Mobil Chemical Company
Attn: Robert Brown
PO Box 250
Edison, New Jersey 08817

Mobil Oil Corporation
Corporate Products Dept.
Attn: D. P. Osterhout
150 East 42nd Street
New York, New York 10017

Mobil Research & Development Corp.
Attn: Dave Barton
Paulsboro, New Jersey 08066

Monsanto Company
Attn: Richard Green
800 North Lindberg Boulevard
St. Louis, Missouri 63166

Monsanto Company
Industrial Chemicals Division
Attn: F. H. Langenfeld
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166

Monsanto Research Corp.
Attn: Library
Station B, Box 8
Dayton, Ohio 45407

Northrop Corporation
Aircraft Division
Attn: Library - H. W. Jones
3901 West Broadway
Hawthorne, California 90250

North American Rockwell
Rocketdyne Division
Attn: L. J. Rainey - Head Librarian
6633 Canoga Avenue
Canoga Park, California 91304

North Carolina State University
Attn: Dean Earl G. Droessler
Research Administration
Raleigh, North Carolina 27650

Oak Ridge National Laboratory
Union Carbide Corporation
Attn: A. G. Grindell
PO Box Y
Oak Ridge, Tennessee 37830

The Pennsylvania State University
Dept. of Chemical Engineering
Attn: Dr. E. E. Klaus
108 Fenske Laboratory
University Park, Pennsylvania 16802

PPG Industries, Inc.
Tribology Lab., Engineering Div.
Attn: H. R. Gorman
PO Box 11472
Pittsburgh, Pennsylvania 15238

Pratt & Whitney Aircraft Group
Florida Research & Development Ctr.
Attn: Librarian
PO Box 2691
West Palm Beach, Florida 33402

Pratt & Whitney Aircraft
Attn: R. P. Shevchenko/E83S-4
400 Main Street
E. Hartford, Connecticut 06108

Pratt & Whitney Aircraft
Attn: Library (L. T. Kress)
400 Main Street
E. Hartford, Connecticut 06108

Pratt & Whitney Aircraft
Attn: S. Bonifazi
MDL - B08
PO Box 2691
West Palm Beach, Florida 33402

PVO International, Inc.
Attn: Al Marcelis
416 Division Street
Boonton, New Jersey 07005

Rennsselaer Polytechnic Institute
Attn: Mr. F. F. Ling
Department of Mechanics
Troy, New York 12181

Rochester Institute of Technology
Dept. of Mechanical Engineering
Attn: Dr. Neville Rieger
Gleason Professor
Rochester, New York 14623

Rohm & Haas Company
Petroleum Chemicals Dept.
Attn: Mike Pohorilla
Independence Hall West
Philadelphia, Pennsylvania 19105

Rose-Hulman Inst. of Technology
Attn: John J. Coy
Terre Haute, Indiana 47803

Royal Lubricants Company
Attn: O. M. Ballentine
River Road
East Hanover, New Jersey 07936

Shaker Research Corporation
Attn: J. M. McGrew
Northway 10 Executive Park
Ballston Lake, New York 12019

Shell Development Company
Westhallow Research Center
Attn: J. W. Armstrong
PO Box 1380
Houston, Texas 77001

Shell Oil Company
Attn: J. E. Lauck
One Shell Plaza
PO Box 2463
Houston, Texas 77001

Shell Oil Company
Attn: R. J. Muller
One Shell Plaza
PO Box 2463
Houston, Texas 77001

SKF Industries, Inc.
Engineering & Research Center
Attn: J. Y. Liu
1100 First Avenue
King of Prussia, Pennsylvania 19406

SKF Industries, Inc.
Attn: L. Sibley
Engineering & Research Center
1100 First Avenue
King of Prussia, Pennsylvania 19406

SKF Industries, Inc.
Attn: Mr. R. E. Maurer
1100 First Avenue
King of Prussia, Pennsylvania 19406

Southwest Research Institute
Attn: B. B. Baber
722- Culebra Road
San Antonia, Texas 78284

Southwest Research Institute
Attn: J. P. Cuellar, Jr.
6220 Culebra Road
San Antonio, Texas 78284

Southwest Research Institute
Attn: Institute Library
6220 Culebra Road
San Antonio, Texas 78284

Sperry Rand Corporation
Vickers Division
Attn: Mr. Sam Jamieson
Engineering Library
Troy, Michigan 48084

Split Ballbearing
Division of MPB Corporation
Attn: Mr. C. A. Griffiths
Highway Four
Lebanon, New Hampshire 03766

Stauffer Chemical Company
Specialty Chemical Division
Attn: Harold W. Adams
Westport, Connecticut 06880

Stauffer Chemical Company
Eastern Research Center
Attn: Dr. P. E. Timony
Dobbs Ferry, New York 10522

Sundstrand Aviation
Dept. 767L
Attn: Engineering Library
4747 Harrison
Rockford, Illinois 61101

Sun Oil Company
Research & Development Dept.
Attn: Library
Marcus Hook, Pennsylvania 19061

Technological Institute
Attn: H. S. Cheng
Dept. of Mechanical Engr.
2145 Sheridan Road
Evanston, Illinois 60201

Tenneco Chemicals, Inc.
Organics & Polymers Div.
Attn: Library
PO Box 365
Piscataway, New Jersey 08854

Texaco, Inc.
Attn: J. P. Covell
PO Box 509
Beacon, New York 12508

Texaco. Inc.
Texaco Research Center
Attn: Tech. Literature Section
PO Box 509
Beacon, New York 12508

The Timken Company
Physical Laboratories
Attn: Mr. Pete Orvos
1835 Dueber Avenue, SW
Canton, Ohio 44706

The Timken Company
Research Library
Attn: A. T. Brown
Canton, Ohio 44706

The Torrington Company
Attn: Mr. W. L. Bowen
59 Field Street
Torrington, Connecticut 06790

TRW, Inc.
Engineering Library, T/M 3417
23555 Euclid Avenue
Cleveland, Ohio 44117

Union Carbide Corporation
Attn: Tech. Librarian
PO Box 24166
1500 Polco Street
Indianapolis, Indiana 46224

Union Carbide Corporation
Chemicals & Plastics Div.
Attn: Walter H. Jogwick
PO Box 8361
South Charleston, West Virginia 253033

Union Carbide Corporation
Chemicals & Plastics
Attn: R. Cupper, Chemicals Bldg.
PO Box 65
Tarrytown, New York 10591

United Aircraft Corporation
Hamilton Standard Division
Attn: Library
Windsor Locks, Connecticut 06096

University of Virginia
Dept. of Mech. Engineering
Attn: Dr. E. J. Gunter, Jr.
Charlottesville, Virginia 22903

Westinghouse Electric Corp.
R&D Laboratories
Attn: Research Library
Beulah Road, Churchill Borough
Pittsburgh, Pennsylvania 15235

Williams Research Corporation
Attn: Lydia Johnstone (Librarian)
2280 West Maple Road
Walled Lake, Michigan 48088

AFAPL/POP-1 (Mr. B. L. McFadden, Jr.)
WPAFB, Ohio 45433

ASD/ENJZ
WPAFB, Ohio 45433

AFAL/TSR
WPAFB, Ohio 45433

AFAPL/CCN
WPAFB, Ohio 45433

AFAPL/STINFO
WPAFB, Ohio 45433 (2 copies)

AFAPL/POP-3/K. E. Binns
WPAFB, Ohio 45433

AFAPL/SFL/H. F. Jones (30 copies)
WPAFB, Ohio 45433

AFML/MBT
WPAFB, Ohio 45433

AFAPL/XP
WPAFB, Ohio 45433

FID/PORS/B. Burns
WPAFB, Ohio 45433

FTD/PDTA-4
WPAFB, Ohio 45433

AF Rocket Propulsion Lab.
Attn: L. Tepe/LKDS
Edwards AFB, California 93523

AFSC/DLF
Andrews AFB, DC 20334

AFSC/DLFP
Directorate of Laboratories
Andrews AFB, Maryland 20331

Air University Library
Maxwell AFB, Alabama 36112

DDC/TCA (2 copies)
Cameron Station
Alexandria, Virginia 22314

SAALC/MMEP/D. G. Harris
Kelly AFB, Texas 78241

SAALC/SFQT
Kelly AFB, Texas 78241

HQ USAF/RDPDT/Mr. A. Eaffy
Washington, DC 20330

Commander
U.S. Army Aviation Systems Command
Attn: AMSAV-EQP (Ralph Tyson)
PO Box 209
St. Louis, Missouri 63166

Director Applied Technology Lab.
U.S. Army Research & Technology Labs.
Attn: DAVDL-EU-ATP/Mr. Allen Royal
Ft. Eustis, Virginia 23604

Director Eustis Directorate
U.S. Army Air Mobility R&D Lab.
Attn: SAVDL-EU-RM (Mr. R. L. Campbell, Sr.)
Ft. Eustis, Virginia 23604

U.S. Army Weapons Command
Watervliet Arsenal
Attn: Dr. R. S. Montgomery
SWEWV-RDR-PS
Watervliet, New York 12189

U.S. Army Weapons Command
Research Directorate
Attn: SWERR-R-ML
Rock Island, Illinois 61201

U.S. Army, Frankford Arsenal
Pitman-Dunn Laboratory
Fluids & Lubricants Branch, L6000
Attn: Joseph Messina
Philadelphia, Pennsylvania 19137

Commander
USA Mobility Equipment R&D Command
Attn: DRDME-GL (M. E. Lepera)
Fort Belvoir, Virginia 22060

EUSTIS Directorate
USAAMRDL/Propulsion Division
Attn: Roger G. Furgurson/SAVDL-EU-PP
Fort Eustis, Virginia 23604

Naval Air Propulsion Center
Attn: Mr. Ray Valori
Fuels, Lubs. & Power Drive
PO Box 7176
Trenton, New Jersey 08628

Naval Air Propulsion Center
Administrative Department
Attn: W. Hawk - ADI
PO Box 7176
Trenton, New Jersey 08628

Naval Air Propulsion Test Center (2 cys)
Attn: PE72/A. L. Lockwood
PO Box 7176
Trenton, New Jersey 08628

Naval Air Rework Facility
Aeron Engrg. Dept.
Attn: Mr. Joe S. Cunningham, Jr.
Marine Corp Air Station
Cherry Point, North Carolina 28533

Naval Air Systems Command
Attn: Mr. Sam Goldberg
Code: AIR 52031
Washington, D.C. 20361

Naval Air System Command
AIR 53645
Washington, D.C. 20361

Naval Air Systems Command
Attn: AIR 330
Washington, D.C. 20360

Naval Air Systems Command
Attn: P. R. Stone
AIR 52032
Washington, D.C. 20360

Naval Air Development Center
Code MAEX
Attn: Mr. Leon Stallings
Warminster, Pennsylvania 18974

Naval Research Laboratory
Attn: Harold Ravner
Code 6177
Washington, D.C. 20375

Naval Research Laboratory
Chemistry Div.
Surface Chemistry Branch
Attn: V. G. Fitzsimmons, Code 6179
Washington, D.C. 20390

Naval Ship Research & Dev. Ctr.
Annapolis Laboratory
Attn: Mr. Nathan Glassman
Code 2831
Annapolis, Maryland 21402

Naval Ship Research & Development Ctr.
Library - Code 5641
Bethesda, Maryland 20034

Office of Naval Research
Code 463 (Lt. Richard S. Miller)
Arlington, Virginia 22217

Office of Naval Research
Code 438
Attn: Mr. S. Doroff
800 N. Quincy Street
Arlington, Virginia 22217

NASA Headquarters
Attn: Joseph Maltz
Code RWM
Washington, D.C. 20546

NASA-Langley Research Center
ADV Supersonic Technical Office
Attn: Mr. Charles H. McLellan
Mail Stop 184A
Hampton, Virginia 23365

NASA-Lewis Research Center
Fluid Systems Components Div.
Attn: William Loomis, MS 23-2
2100 Brookpark Road
Cleveland, Ohio 44135

NASA-Lewis Research Center
Attn: Edmond E. Bisson, MS 5-3
21000 Brookpark Road
Cleveland, Ohio 44135

NASA-Lewis Research Center
Mail Stop 6-1
Attn: Dr. David Fleming
21000 Brookpark Road
Cleveland, Ohio 44135

NASA-Lewis Research Center
Attn: Paul Kerwin, MS 500-210
21000 Brookpark Road
Cleveland, Ohio 44135

NASA-Lewis Research Center
Attn: Richard Parker, MS 6-1
21000 Brookpark Road
Cleveland, Ohio 44135

NASA-Lewis Research Center
Attn: Erv Zretsky, MS 6-1
21000 Brookpark Road
Cleveland, Ohio 44135

Defense Fuel Supply Center
Directorate of Tech. Operations
Attn: Dr. J. A. Krynitsky
Cameron Station
Alexandria, Virginia 22314

Defense Supply Agency
Office of Technical Services
Dr. John A. Krynitsky, Director
Camerson Station
Alexandria, Virginia 22314

Department of Transportation
Library Service Div.
FOB-10A, TAD-494.6
800 Independence Ave., S.W.
Washington, D.C. 20591

FAA HQ
CAD-1
H. Rochen
800 Independence Ave., S.W.
Washington, D.C. 20591

Federal Aviation Administration
Propulsion Branch, AFS-140
800 Independence Avenue, S.W.
Washington, D.C. 20591

US Atomic Energy Commission
Div. of Reactor Development &
Technology
Attn: Nicholas Grossman, F-309
Washington, D.C. 20545

☆U.S.Government Printing Office: 1979 — 657-002/451