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GRADUATE COLLEGE

VIBRATIONAL SPECTRA OF CRYSTALS OF COMPOUNDS WITH METHYLENE CHAINS

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

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Norman, Oklahoma

1965

VIBRATIONAL SPECTRA OF CRYSTALS OF

COMPOUNDS WITH METHYLENE CHAINS

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PREFACE

The study of vibrational frequencies of crystals of compounds with methylene chains requires a knowledge of both the polarized infrared spectra and the Raman spectra. Instrumentation is available which allows the polarized infrared spectra to be obtained of small single crystals of these compounds. However, the present techniques of obtaining Raman spectra of crystalline powders usually do not yield good results.

Because of their importance, the compounds containing methylene chains have been studied extensively. But only for a few have all fundamental vibrational frequencies been assigned with any degree of certainty. More often than not, Raman data for such compounds in their crystalline state are not available or are rudimentary.

The research presented in this dissertation represents the terminal report of a long series of extensive investigations on the crystalline state of compounds containing methylene chains undertaken by Professor J. Rud Nielsen and his students.

In order to obtain more complete Raman data on compounds containing methylene chains, considerable time was spent on the development of a Raman illumination system for powdered crystalline samples. The development of such a system is given in detail in Part I. Numerous examples of the capability of the system to produce good Raman spectra of both crystalline powders and solid polymers are given.

In Part II of this report a vibrational study of the normal dicarboxylic acids, $HOOC(CH_2)_nCOOH$, is presented. The Raman data have been obtained for malonic (n = 1), succinic (n = 2), glutaric (n = 3), adipic (n = 4), pimelic (n = 5), suberic (n = 6), azelaic (n = 7), sebacic (n = 8) and tetradocanedioic (n = 12) acids. The polarized infrared spectra in the region from 1800 to 400 cm^{-1} have been obtained for single crystals of all of these acids except malonic and succinic acids. From the data on this series of acids the development of certain vibrational band series can be observed. Furthermore, the effect of different crystal forms on the infrared spectrum has been studied on pimelic acid. The vibrational spectra of the dicarboxylic acids have been interpreted in terms of the known molecular and crystalline structures.

The author wishes to express his sincere appreciation to Professor J. Rud Nielsen for his constant guidance and limitless patience during the period of this investigation.

The author is also indebted to Professor D. Van der Helm for the x-ray diffraction studies and enlightening discussions concerning the structure of several crystals. Acknowledgement is due Norman Alexandre for his technical advice and patience during the perfection of the focal-point Raman lamp.

Finally, for her cheerfulness and ever present encouragement, the author is deeply grateful to his wife.

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PART I. RAMAN SPECTROSCOPY OF CRYSTALLINE POWDERS AND POLYMERS

CHAPTER I

PREVIOUS RAMAN SPECTROSCOPY TECHNIQUES FOR SOLIDS

Introduction

Information on normal vibrations of molecules may be obtained from the interaction of the molecules with electromagnetic radiation. If the dipole moment of a molecule changes during a normal vibration, there can be an absorption of electromagnetic radiation at the resonant frequency. The frequencies associated with normal vibrations of molecules are found in the infrared region of the electromagnetic spectrum. If there is no change of dipole moment during a normal vibration, it cannot be observed in the infrared absorption spectrum.

A transition between the vibrational states of a molecule can often be revealed in the light scattered by the molecule. This phenomenon was first observed by C. V. Raman[1] in 1928 and has become known as the Raman effect. In the Raman effect the light scattered from a group of molecules is found to contain frequencies different from the incident frequency. The differences between the incident frequency and these modified frequencies equal certain normal vibration frequencies of the molecule. Both the classical and quantum mechanical explanations of this

phenomenon have been given adequately in an article by Placzek.[2] He has shown that Raman scattering can occur only when there is a change in the polarizability of a molecule during a normal vibration.

Thus, a normal vibration of a molecule may be observed in either infrared absorption or the Raman spectrum or in both; it is also possible for a vibration to cause no change in either the dipole moment or in the polarizability and therefore not be observable in either infrared absorption or the Raman spectrum. Whether or not a given normal vibration will be active or inactive with regard to infrared absorption or Raman scattering depends upon the symmetry of the vibration in a manner which is well understood.[3,4,5]

If the symmetry point group to which a molecule belongs is known, then group theoretical considerations allow the normal vibrations of the molecule to be classified according to symmetry species and their activities to be ascertained. If the molecule possesses an inversion center as a symmetry element, then the infrared- and Raman-active normal vibrations will be mutually exclusive. In such cases, both the Raman and infrared data must be obtained in order to give complete information on the normal vibrations of the molecule.

While infrared spectroscopy has yielded information concerning molecular and crystalline structure of many materials in the solid state,[6] Raman spectroscopy has not yet become a very useful tool in the investigation of solid substances. This is primarily because it is difficult to obtain Raman data for solids. Nielsen[7] has reviewed the difficulties in obtaining Raman spectra of polymers.

In the past, extensive Raman data has been obtained only for

solids which could be grown into large crystals (e.g., quartz, oxalic acid) or solids which could be fused into transparent samples (e.g., polystyrene). Menzies[8] has given an excellent bibliography of the Raman effect in solids up to 1953. Raman date on solids which are available only as crystalline powders or translucent solids are generally rudimentary or non-existent. Krimm[9,10] has pointed out this absence of Raman data for solid polymers and the problems posed by the absence of such data.

During the last five years the author has investigated a number of Raman illumination systems in an effort to make the experimental task of gaining Raman data on crystalline powdered samples more feasible. These various systems, their modifications and limitations, and their relationship to previous work will be discussed briefly. The final Raman illumination system for crystalline powders and solids, its performance and limitations, will be discussed in detail.

General Experimental Technique

To obtain Raman data, the sample is illuminated by an intense source of monochromatic light and the scattered light is observed with the aid of a fast spectrograph. The Rayleigh scattering produces a strong spectral line at the wavelength of the incident light. On either side of the Rayleigh scattered incident line the sample will produce Raman modified bands. The Raman data may be obtained from the spectrograph either photographically or photoelectrically.

The photoelectric spectrograph is capable of recording the Raman data rapidly, but is not as flexible as the photographic spectrograph. Furthermore, the photographic instrument with its ability to integrate

the Raman illumination over long periods of time yields a higher ultimate sensitivity than the photoelectric instrument. However, improvement of the illumination system for solids now used with photoelectric instruments may lead to a sensitivity equal to that of photographic instruments.

The proper design of a Raman illumination system must take into consideration the theoretical factors governing the intensity of the Raman scattered light. The intensity of Raman scattered light from an arbitrary anisotropic crystal has been shown to be proportional to (1) the fourth power of the Raman scattered frequency, (2) the intensity of the exciting light, and (3) the amount of sample which can be utilized effectively.[11] The first two factors are determined by the choice of the Raman exciting source, since the frequency of the Raman scattered light is dependent upon the exciting frequency and the frequency of the normal vibration involved in the scattering process. The third factor is governed by the nature of the sample and the geometry of the illumination system.

Ideally a Raman illumination system consists of a geometrical arrangement which is capable of illuminating a concentrated sample with radiation from an intense, monochromatic source whose wavelength is as short as feasible. The exciting frequency must not be so high that it will be absorbed by electronic transitions. That is, the energy associated with the exciting frequency, ν_e, must be less than the forbidden electronic energy gap, E_g, characteristic of the sample under study.

The intensity of Raman scattered light is of the order of 10^{-6} or less of that of the incident exciting light.[12] Even with samples known

to be good Raman scatterers (e.g., carbon tetrachloride, naphthalene) proper illumination is important. A typical illumination system used for both liquids and solids is shown in Fig. I-1.

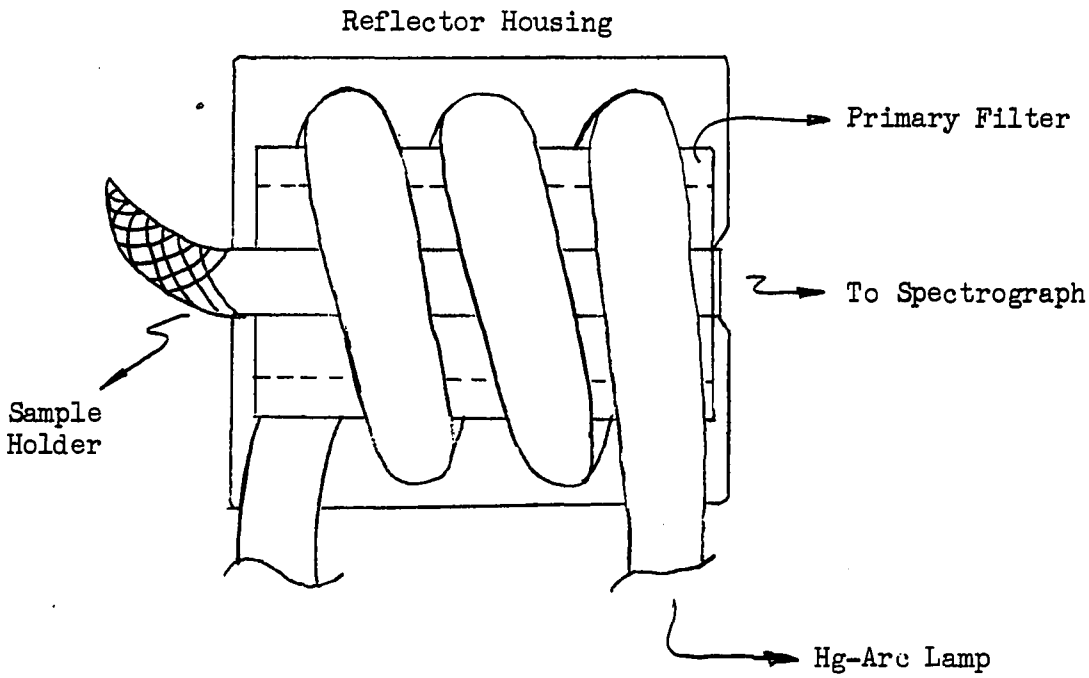


Figure I-1.

The Raman exciting line must be appreciably diminished prior to its entry into the spectrograph to prevent excessive darkening of the photographic plate adjacent to the exciting line position due to over-exposure. Effective removal of the exciting line allows Raman data to be obtained for low frequency normal vibrations, i.e., 0 to 200 cm^{-1}. Observation at right angles to the source illumination decreases the amount of the exciting light reaching the spectrograph, but secondary filtering is used often to decrease the amount still further.

The choice of an intense, monchromatic source has been limited to arc-lamps until the recent advent of lasers. The mercury-arc lamp provides several intense lines in its spectrum, of which the most intense are at 2537, 4046, 4358 and 5461 A.[13] The 2537 A line due to its shorter wavelength possesses a factor of approximately ten in Raman excitation efficiency over the 4358 A line for equal illumination intensity. The Rayleigh scattered 2537 A line is eliminated easily by absorption in a Hg-vapor cell, since this line represents a resonance transition.

Because of these advantages the 2537 A line has been used for Raman excitation in solids. A system based on a design by Rasetti[14] has been in use in Bangalore, India since 1943.[15] This illumination system appears unexcelled for observation of Raman bands below 200 cm^{-1} and has been used recently to obtain Raman data on several normal dibasic carboxylic acids.[16,17]

However, excitation by the 2537 A line has certain distinct disadvantages. Quartz optics must be used throughout the illumination system and spectrograph. The speed and dispersion of quartz spectrographs are generally lower than high quality glass prism and grating Raman spectrographs. Since the 2537 A line is easily absorbed by Hg-vapor, special magnetically-controlled, quartz mercury lamps must be utilized to prevent appreciable absorption of this line in the lamp. Many samples absorb in this spectral region, that is, many samples possess a forbidden electronic energy gap, E_g, less than the $\sim$5 ev energy associated with the 2537 A line. Furthermore, the 2537 A line can cause fluorescence of certain samples which can obscure the Raman bands and can also cause photo-decomposition of many samples.

For these many reasons the 2537 A line has not been used frequently as a Raman excitation source. The lines at 4046 and 4358 A have been used predominently for the study of the Raman effect in solids as well as liquids. For certain colored samples and samples which are fluorescent, the Hg-5461 A[18] line or various other long wavelength lines[19,20] have been used for Raman excitation. Further development of lasers[21,22,23,24] as a Raman source may alleviate the problem caused by colored samples and samples which are fluorescent under blue or violet light.

Previous Raman Systems for Crystal Powders

At this time the Hg-4358 A line appears to be the best source of intense monochromatic radiation for Raman excitation in most solids. Recently, Nielsen and Woollett[25], Tobin[26], and Moser and Stieler[27] have done extensive work in developing successful crystalline powder Raman illumination systems utilizing the Hg-4358 A line. Moser and Stieler have given an excellent appraisal of earlier work and an extensive bibliography.

In the region near 4800 A of a Hg-spectrum an emission continuum of Hg_2 is found.[28] This continuum tends to obscure the Stokes - Raman bands excited by the 4358 A line. It is desirable, therefore, to isolate the 4358 A line, eliminating both this continuum and other Hg-lines. The 4358 A line can be sharpened and the continuum largely surpressed simply by water cooling the Hg-electrodes. The effective cooling of the electrodes assures that the Hg-vapor pressure remains sufficiently low such that Hg_2 molecules are not readily formed. However, this continuum persists and must be supressed still further by filtering when the weak Raman spectra

of many solids are to be studied.

The illumination system used by Nielsen and Woollett[25] for the Raman study of n-paraffins and polyethylene is similar to that shown in Fig. I-1. The illumination system consisted of a single-helical coil, water-cooled electrode Hg-lamp mounted in an aluminum housing with polished inner surfaces shaped so as to concentrate a maximum of light on an 8 mm, diameter Raman tube placed coaxially with the lamp. An annular filter jacket filled in most cases with a sodium nitrite solution was placed between the lamp and the sample. The lamp barrel and filter were cooled by blowing air through the assembly. The sodium nitrite solution served to suppress the 4047 A line so as to eliminate Raman excitation by this line.

No effort was made to eliminate the continuum prior to illuminating the sample or to suppress the exciting line prior to its entry into the spectrograph. Typical exposure times ran over 100 hours and considerable background was encountered. The background was due primarily to fluorescence of the sample, but in the case of the n-paraffins it is highly probable that the continuum of the lamp also added to the background. Darkening of the photographic plate in the region of low frequency Raman bands (700 cm^{-1}) was evident due to overexposure of the exciting line.

Tobin[26] improved this system considerably by introducing a filtering system to isolate the 4358 A line and using interference filters in reflection to suppress the 4358 A line prior to its entry into the spectrograph. Reflecting the Raman radiation from interference filters transmitting the 4358 A line was first introduced by Brandmüller.[29] Tobin's

system, similar to that shown in Fig. I-1, used a Toronto-type Hg-lamp with four helical turns. He used an elaborate chemical filter system consisting of a saturated sodium nitrite solution, a 0.95 molar solution of $PrCl_3$ and NH_4 ethylene diaminetetraacetate, and a solution of ethyl violet taken up on uncoated cellophane. This filter system transmits approximately 40% of the 4358 A line while suppressing the long-wavelength continuum.

The sample was mounted coaxially with the lamp in a tube of 4 mm internal diameter, tapering to a 2 mm internal diameter in a distance of 2 cm. The Raman radiation was collimated, reflected from two interference filters transmitting 4358 A radiation, and focussed on the spectrograph slit by lenses matching the spectrograph cone of aperture.

In exposures of 3 to 6 hours, Tobin confirmed the Raman bands of Marlex 50 found by Nielsen and Woollett, but added no new information. He noted that the background was considerable and stated that the fluorescence was the limiting factor for studies on polyethylene and polypropylene. He also attempted to obtain the Raman spectrum of polytetrafluoroethylene but was unsuccessful.

Tobin indicated that the interference filter 4358 A rejection system worked well and that except for grating ghosts the spectra were clear down to the exciting line. He pointed out the possibility of observing the lattice vibrations of crystals with such a system. However, in none of Tobin's work are Raman lines observed below 800 cm^{-1} and in his spectrum of isotactic polypropylene[30] there is evidence of an increasing background from 800 cm^{-1} down to the exciting line.

Tobin analyzed the geometry of the Toronto-arc with a coaxially

mounted sample and a Brandmüller source with collimator lens and various sample shapes. He concluded that the Brandmüller source delivers only 10% of the illumination to the sample that would be received from a Toronto-arc. He calculated that for a back-illuminated sample, used frequently with a Brandmüller source, there is an optimum thickness given by $x = 1/k$, where k is the specific extinction of the sample. For the coaxially-mounted, side-illuminated sample he found no optimum length nor diameter. He did not consider the effect of masking a small area at the end of the Raman tube in order to decrease the stray illumination scattered into the spectrograph cone of aperture.

A Tobin illumination system was constructed by the author and used with a Hilger E612 spectrograph with both f/1.5 and f/5.6 cameras and Kodak 103a-O photographic plates. Both single- and double-helical coil Toronto lamps operating at approximately 12 amperes were used. While the exposure time was found to be short, the background was always the limiting factor. By shielding a short part of the front of Raman tube the amount of unmodified mercury light emerging from the Raman tube window was minimized and the background decreased slightly.

However, the extent of the background did not seem to vary with sample fluorescence and a sample of boric acid with low fluorescence was found to have a high background. A glass tube, sand-blasted to make it translucent similar to a solid sample, was placed in the sample position and the resultant exposure showed a background which could not have been caused by fluorescence. It was concluded that even as efficient as Tobin's chemical filters were, the continuum from the Hg-lamp was still a major problem. Various chemical filters and more efficient techniques of cooling

the helical barrel of the lamp were tried but no improvement was noted in the background.

During this period it was found that while the f/1.5 camera on the Hilger E6I2 spectrograph allowed exceedingly short exposures, its low dispersion and its apparent stray scattering of radiation made its usefulness for Raman work doubtful.

The 4358 A rejection system using two Bausch and Lomb interference filters transmitting 4358 A radiation was found to be lacking due to the poor quality of the filters. A rejection system employing Baird-Atomic, Inc. interference filters transmitting 4358 A radiation was constructed and considerable improvement was found in the elimination of the exciting line. Tobin indicated that he used interference filters peaked to transmit 70% of Hg-4358 A at an angle of incidence of $5^{\circ}46'$ with a half-width of 10 A. The firm which supplied Tobin his filters indicated that they could not produce such a filter and that perhaps the true half-width was 100 A.[31] No firm could be located by the author until very recently which could approach these characteristics.

The Tobin technique was abandoned and an extended arc-lamp consisting of a water-cooled, 20 cm long, 1.5 cm diameter tube with water-cooled electrodes was constructed. The intensity delivered at a point by such a transparent source is proportional to the depth of the source.[26] This lamp is shown in Fig. I-2. It operated with a potential drop of approximately 40 volts and 20 amperes. The windows on the end of the lamp barrel were made of flat pyrex glass. A Baird-Atomic interference filter transmitting approximately 40% of Hg-4358 A was located immediately in front of the lamp and the sample in the form of a disk was placed

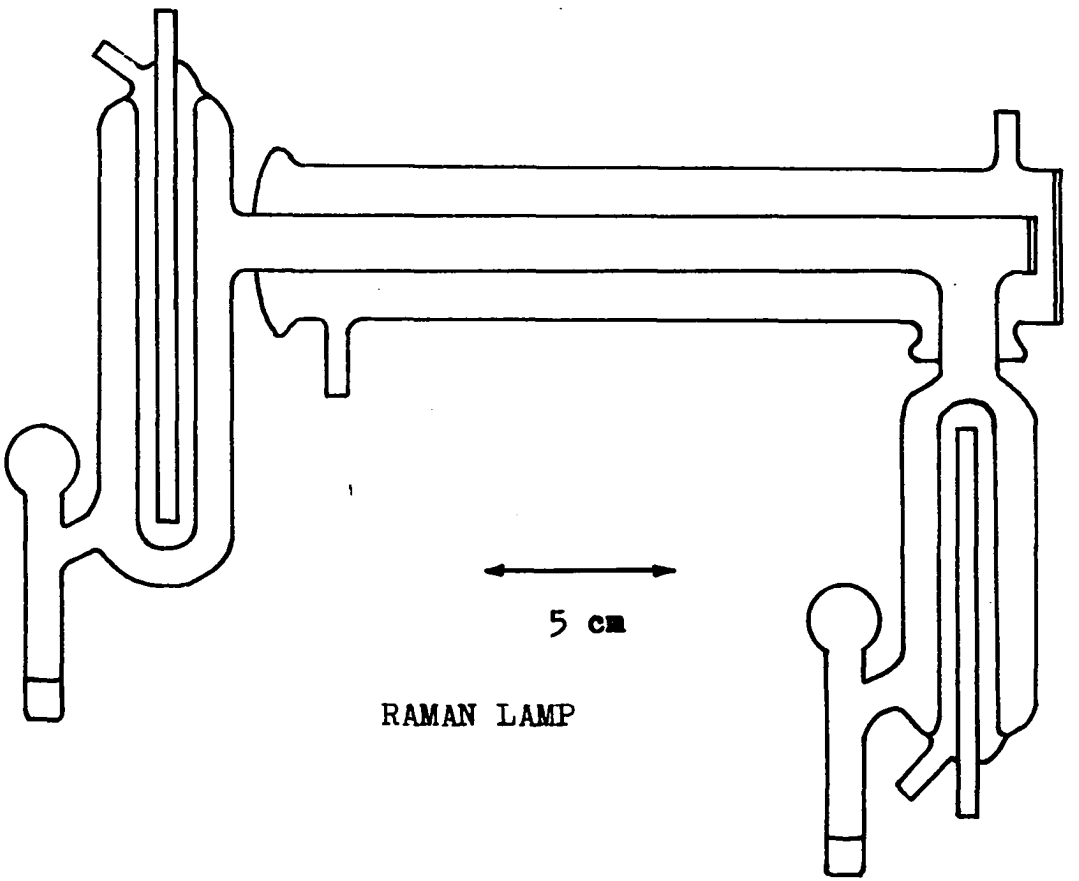


Figure I-2

immediately behind the filter.

The same interference filter rejection system was used, and while the exposure times were slightly increased (3-4 times) for similar samples over the Tobin illumination system, the background was found to be considerably less. The use of the Hg-4047 A line with this system was investigated, but was not found to be practical because of the lack of high transmitting interference filters in this spectral region.

While this system was in the development stage the author's attention was drawn to work done by Moser and Stieler.[27] These authors reviewed previous crystal illumination apparatuses and studied experimentally the various techniques and associated sample geometries. They described an intense low-pressure mercury lamp with a constriction producing a "focal point" of very high luminosity. They compared the different forms of irradiation using powdered naphthalene as a sample and concluded that back irradiation of a pellet or lateral irradiation of a cylindrical Raman tube with conical innersurface ("Kegelkuvette") give the best results.

Moser and Stieler reported, as did Tobin, that theoretically the back-illuminated tablet should have an optimum thickness given by $x = 1/k$. They used no primary filter nor a secondary filter rejection system, although they reported the possibility of using such a scheme. They found that while the optimum tablet thickness gave good Raman data for powdered naphthalene with exposures as short as 8 minutes, measurements could not be made below ~ 500 cm^{-1} because of overexposure of the exciting line. By increasing the thickness by a factor of four and the exposure time by a factor of eight an equivalent exposure was obtained which showed lattice vibrations as low as 13 cm^{-1}.

Using this system Moser and Stieler reported 35 vibrational Raman lines for a tablet of powdered naphthalene between 400 and 3300 cm^{-1}. They did not indicate the length of the longest exposure nor show the spectrum obtained. The spectra they do show indicate an increasing background from approximately 800 cm^{-1} down to the exciting line. These data represent the best Raman spectrum of naphthalene available in the literature.

As good as the Raman data reported by Moser and Stieler are, few papers have appeared which have used their system. Behringer[32] has reported a slight modification of sample irradiation using the focal point lamp. Geppert and Scholz[33] have reported some observations on the focal point lamp and indicate some problems concerning distillation of the mercury from the one electrode to another. Moser[34] reported the possibility of using the focal-point lamp-tablet sample system to make photelectric measurements of Raman bands of solids.

CHAPTER II

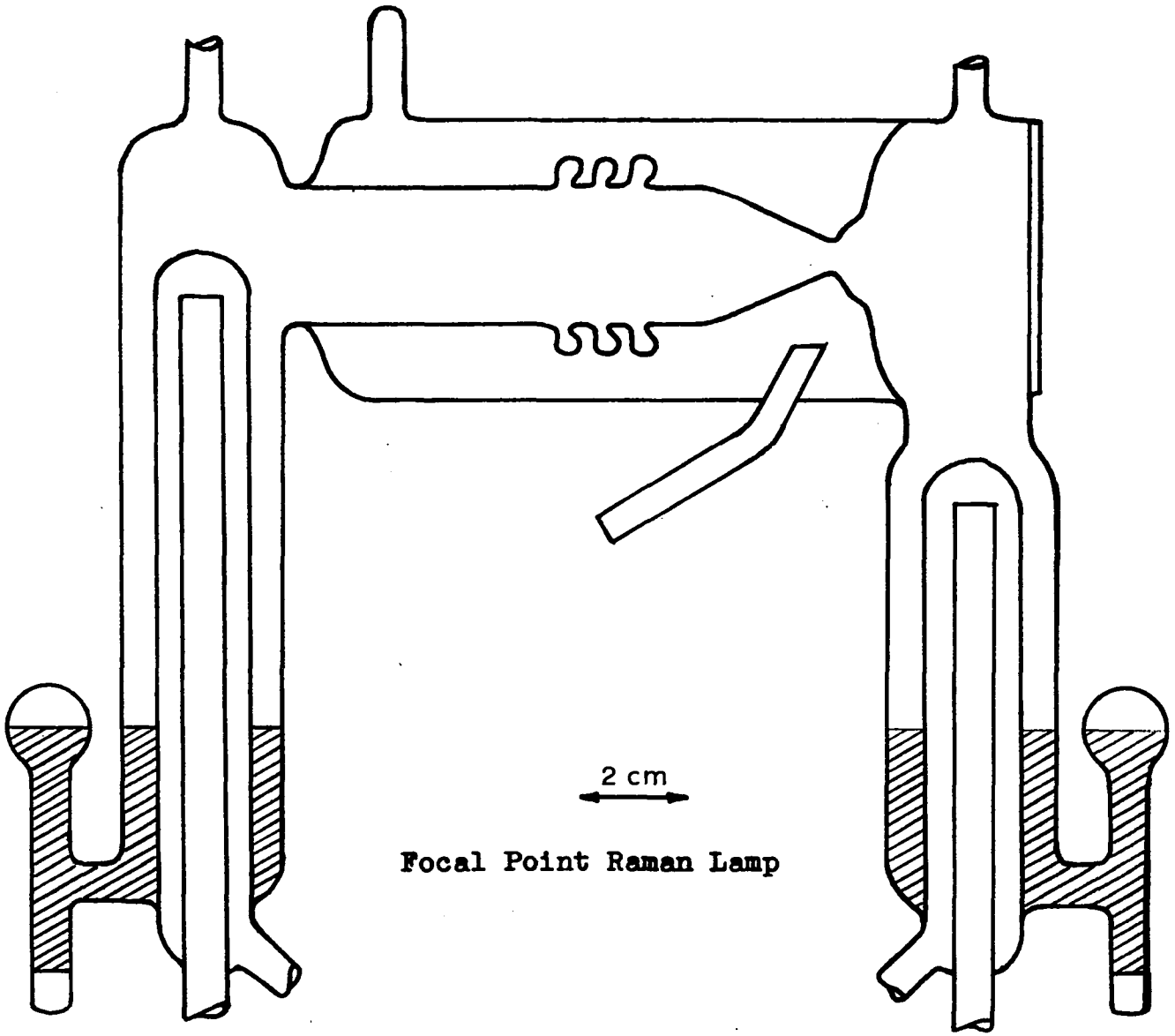
THE FOCAL POINT RAMAN IRRADIATION SYSTEM

Focal-Point Mercury Lamp

Eight lamps representing various modifications of the focal point, low-pressure, Hg-lamp have been constructed. Early designs of this lamp, similar to the original described by Moser and Stieler,[27] were found to be short-lived. The final design of the lamp is shown in Fig. II-1.

The lamp, constructed entirely of pyrex, consists of two, internally water-cooled mercury electrodes separated by a distance of 28 cm. The diameter of plasma tube connecting the two electrodes is 25 mm. This tube is physically constricted or "pinched" to a diameter of 5 mm and then allowed to expand to 52 mm immediately before the front window. This tube is water cooled up to and including the constricted point. The front window of the lamp consists of a flat pyrex disk 52 mm in diameter. In all lamps constructed the distance between the constriction and the window was held to less than 50 mm so that the lamp had an effective aperture of f/1.0 or better for the region around the constriction.

In the early forms of the lamp the constriction was abrupt. The first lamps which operated at approximately 35 volts potential and 15 amperes were found to shatter at the constricted point due to strain after short periods of use. Localized boiling of the cooling water was observed



Focal Point Raman Lamp

Figure II-1

often near the constriction. An effort was made to reduce the thermal shock at the constricted point by using a small piece of Vycor tubing fitted tightly into the constriction. However, cooling of the Vycor tubing by the outer water jacket was insufficient and the Vycor tubing melted away in a period of fifteen minutes. It was found that some of the strain at the constricted point could be reduced by using bellows in the plasma tube and by tapering on one side of the constriction from 25 mm to 5 mm diameter over a length of 25 mm. This does not appear to affect the luminosity at the constricted point. While the strain was reduced at the constriction, breakage of a less violent nature continued to occur.

Normally one water-cools a mercury lamp so as to maintain a low pressure and thereby reduce the background continuum in the Hg-spectrum. It was found experimentally that the focal point Raman lamp must be operated such that the coolest part of the lamp is above 30°C. If the lamp is so operated, then it is long-lived and breakage does not occur. Two lamps have been constructed which have been so operated at 25 amperes and were found to be successfully long-lived. One lamp was operated for a period of 1676 hours and was broken while being examined for possible strains. The last lamp was operated for a period of 1911 hours, has been successfully cleaned and rebuilt, and is now in operation.

Contrary to the darkening of the glass envelope found in most other pyrex Hg-lamps,[35] the window of the focal point lamp was not found to be appreciably darkened after 1911 hours use. However, the darkening in the region of the constriction was heavy.

Operating Characteristic of the Lamp

In the effort to obtain a practical long-lived, focal-point Raman lamp considerable data were taken on the lamp itself. The potential - current relationship was studied by maintaining a constant load across the lamp and a variable resistor in series. Varying the series resistor caused the potential across the lamp to change. Two such potential-current curves for electrode temperatures of 21°C and 35°C are shown in Fig. II-2. These curves were found to change form as a function of the electrode temperature. When the lamp was operated at electrode temperatures below 30°C, voltage surges of the order of 2 volts were observed across the lamp.

If one electrode is made to be the coolest part of the lamp, then the other electrode and water-cooling jacket may be operated at various temperatures above the cool electrode with no apparent affect on the potential-current relationship. Hence, the potential-current relationship is determined by the temperature of the coolest part of the lamp. Measurements with thermocouples showed the temperature of the air-cooled parts of the lamp to be approximately 175°C. A thermocouple mounted in a glass probe in the plasma tube indicated inner wall temperatures from 300°C to 500°C depending on how long the lamp was operated.

Provisions have been made for heating each electrode and the cooling jacket separately. One electrode temperature, the cooler, determines the mercury vapor pressure[36] in the lamp and hence the operating conditions of the lamp. The temperatures of the other electrode and the cooling jacket are adjusted so as to overcome any tendency for distillation of the mercury from one electrode to another. Typically the water

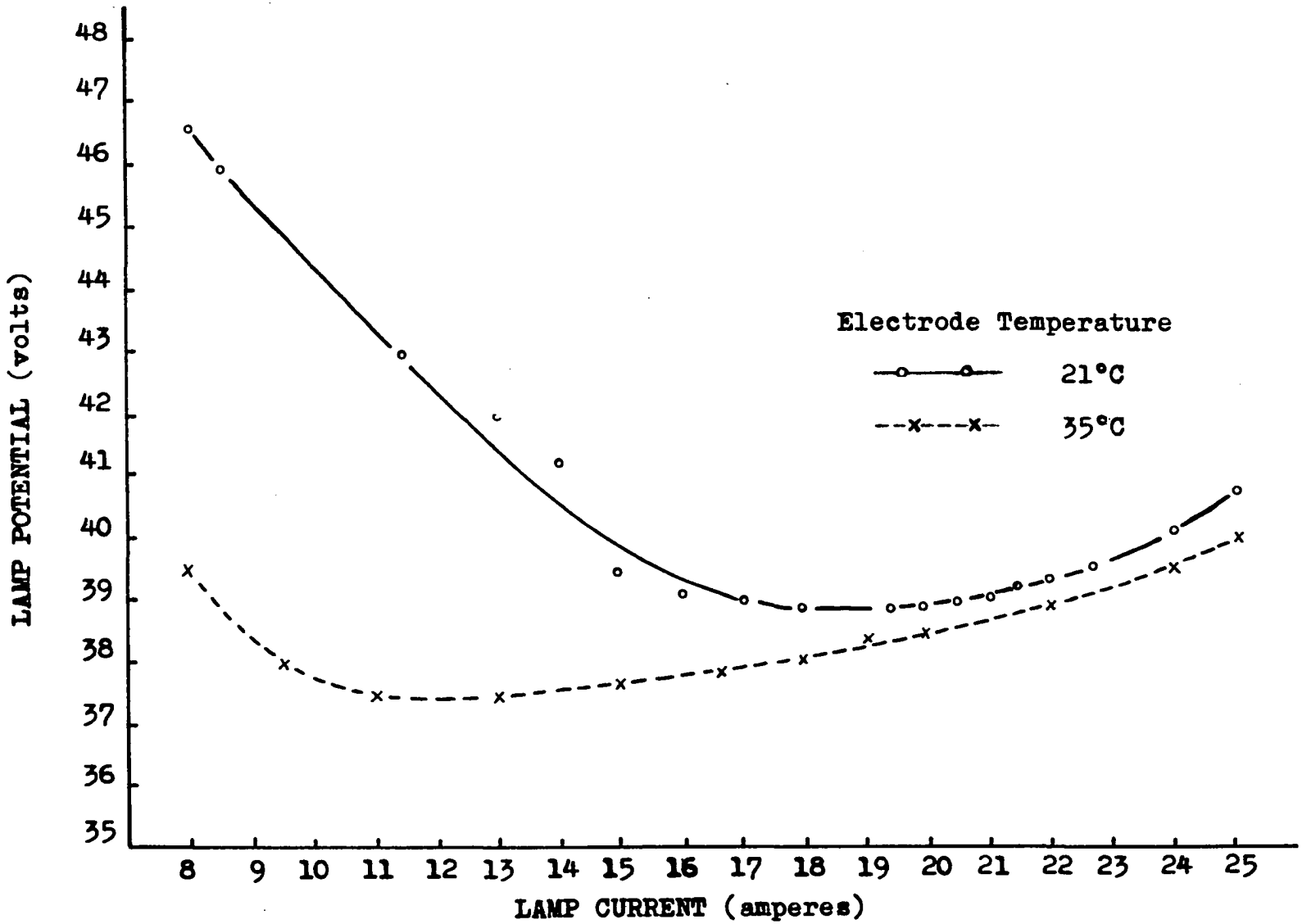

LAMP POTENTIAL (volts)
48
47
46
45
44
43
42
41
40
39
38
37
36
35
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
LAMP CURRENT (amperes)
Electrode Temperature
21°C
35°C

Figure II-2

temperatures for the electrodes are 32°C and 35°C, and 45°C for the water-cooling jacket.

A study of the luminous output of the lamp from the constricted region was made by measuring the current through a CdS cell placed in the sample position. An early study of the light output as a function of current for a low electrode temperature ($\sim 20^{\circ}C$) seemed to indicate that the luminous intensity, of wavelength 4358 A, at the constriction increases very slowly with the current above ten amperes.[7] However, later studies of the luminosity showed the light output of the 4358 A line to vary both as a function of the current and of the electrode temperature. The light output of Hg-4358 A for electrode temperatures of 25°C, 35°C and 45°C is plotted in Fig. II-3 in terms of μ-amperes CdS cell current versus the lamp current. The lamp on which these data were obtained had been operating for 337 hours. The 4358 A intensity was found to increase with the current. The 4358 A output increases as a function of current up to 30 amperes was shown also by the increasing intensity of a given Raman band (1380 cm^{-1}) of a naphthalene sample in a series of 5 minute exposures taken at different lamp currents. The intensity of this Raman band is plotted as a function of current in Fig. II-4.

A study of the luminous intensity of the 4358 A line at currents of 15 and 30 amperes for different electrode temperatures, 20°C to 65°C, did not yield any conclusive data. This is probably because this electrode temperature range corresponds to a mercury vapor pressure change of only one order of magnitude and the intensity of the radiation is a relatively slow changing function of Hg-pressure. No attempt was made to measure the absolute luminous intensity nor to measure what percentage of the visible

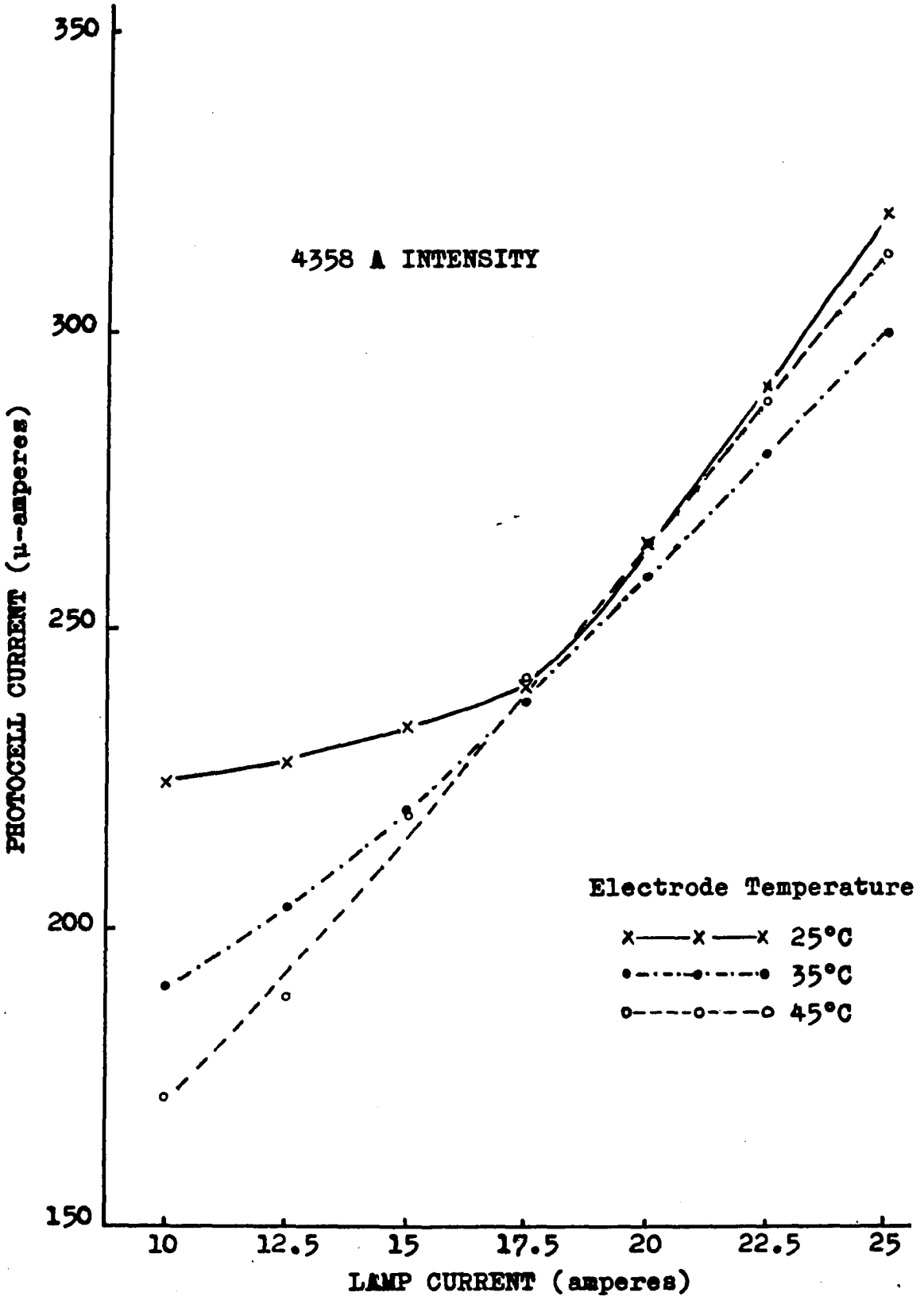

4358 A INTENSITY
PHOTOCELL CURRENT (μ-amperes)
350
300
250
200
150
10
12.5
15
17.5
20
22.5
25
LAMP CURRENT (amperes)
Electrode Temperature
25°C
35°C
45°C

Figure II-3

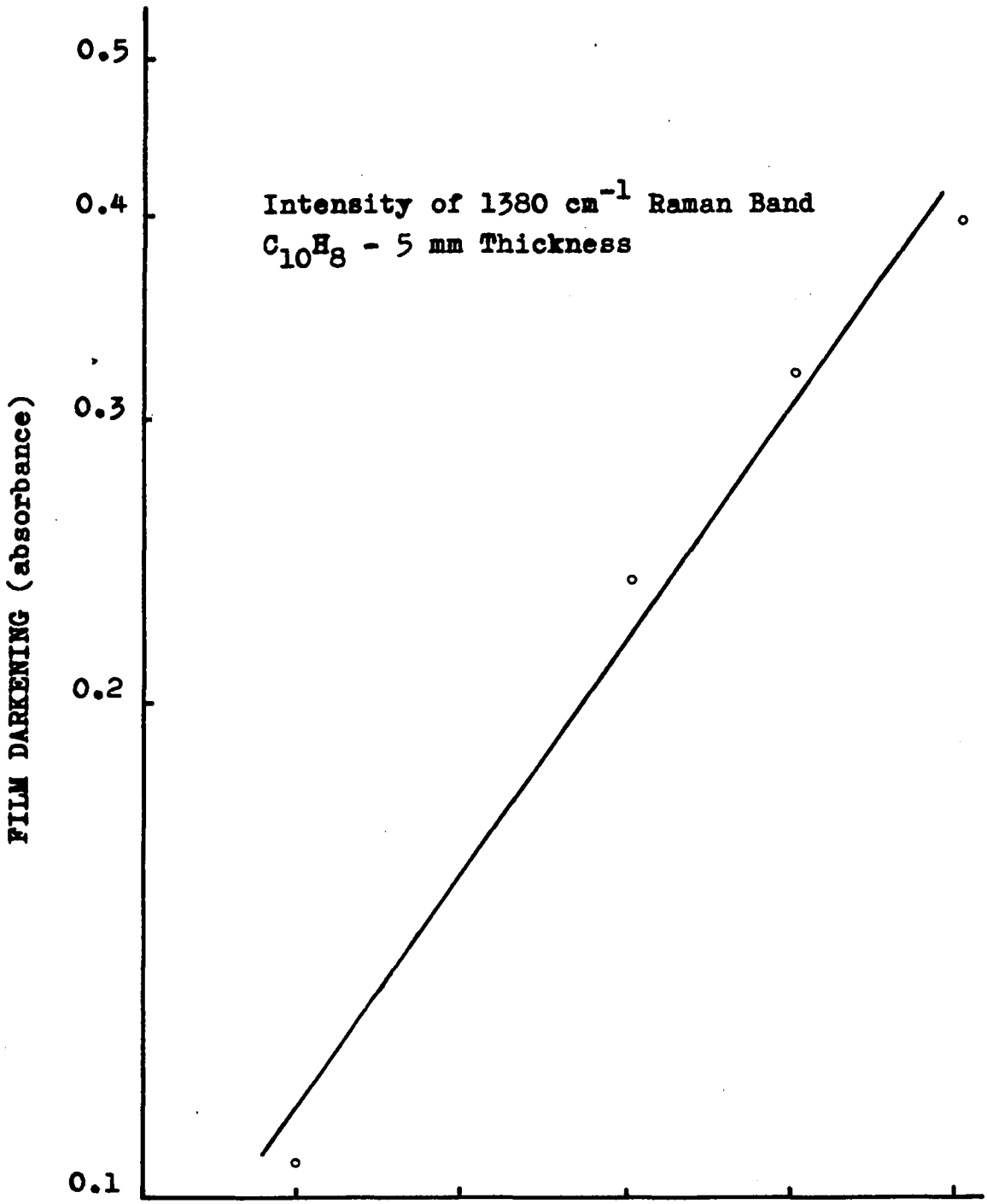

Intensity of 1380 cm^{-1} Raman Band
$C_{10}H_8$ - 5 mm Thickness
FILM DARKENING (absorbance)
0.5
0.4
0.3
0.2
0.1
10
15
20
25
30
LAMP CURRENT (amperes)

Figure II-4

radiation was 4358 A radiation. The relationship between the intensity of the 4358 A line, the current density, and the mercury vapor pressure is probably complicated.[37]

The spectral output of this lamp was found to contain lines not normally observed in the mercury arc spectrum. Measurement of these lines showed most of them to be due to transitions in ionized mercury. The identification of these lines was necessary in order that they not be mistaken for Raman bands. These lines have been measured and tabulated in Appendix I.

Qualitative Explanation of Processes Occurring in the Lamp

These data when examined with what is known concerning gaseous conductors can qualitatively explain the necessity for operating the lamp at a slightly elevated temperature. Both the voltage-current curves and the luminosity curves indicate a possible variation in processes occurring in the lamp at different electrode temperatures. It is fairly well established that the vapor pressure in any part of a mercury vapor lamp does not differ by more than a factor of 2 or 3 from the vapor pressure corresponding to the coolest part of the lamp.[36] Hence the dependence of potential-current curves and the partial dependence of luminosity curves on the coolest electrode temperature is understandable.

Recombination of the positive ions and electrons in the vapor is very unlikely because of the greatest difference in speed with which ions and electrons are moving. Recombination at low pressure must occur either on the walls of the tube or on the electrons. The process of recombination at the walls is not well understood. Apparently, the electrons

come up to the surface and adhere to it, giving up their kinetic energy in the form of heat.[38] This apparent adhering of electrons after recombination at the walls may account for the darkening of the pyrex glass.[39]

When an arc column is reduced in cross-section by gradually decreasing the diameter of the discharge tube, the random-electron current density will increase gradually along the tube and there will be no discontinuity in potential. However, if there is an abrupt or sharply tapered constriction in the tube diameter, there will be an abrupt change in random current density in order to maintain the same drift current. This will be accompanied by the development, at the start of the constriction, of a potential difference sufficiently great to provide additional ionization required by the smaller tube. When the current to a constriction is increased, a point is reached at which the ionization of the vapor in the constriction is nearly complete and a further increase in current is impossible without multiple ionization. Under certain conditions this may result in voltage surges.[40] This phenomenon of ionization and voltage surges has been observed in the focal point Raman lamp and is particularly noticeable at low mercury vapor pressures.

Using the Tonks-Langmuir curve[41] of pressure times radius in cm-mm Hg versus the electron temperature shown in Figure II-5 the electron temperatures for the various regions of the focal-point lamp can be determined as a function of the cooler electrode temperature. Such curves for the constricted and non-constricted regions of the lamp are shown in Figure II-6. Relating these electron temperatures to the experimental data of Killan[42] for wall heating versus electron temperature a qualitative picture

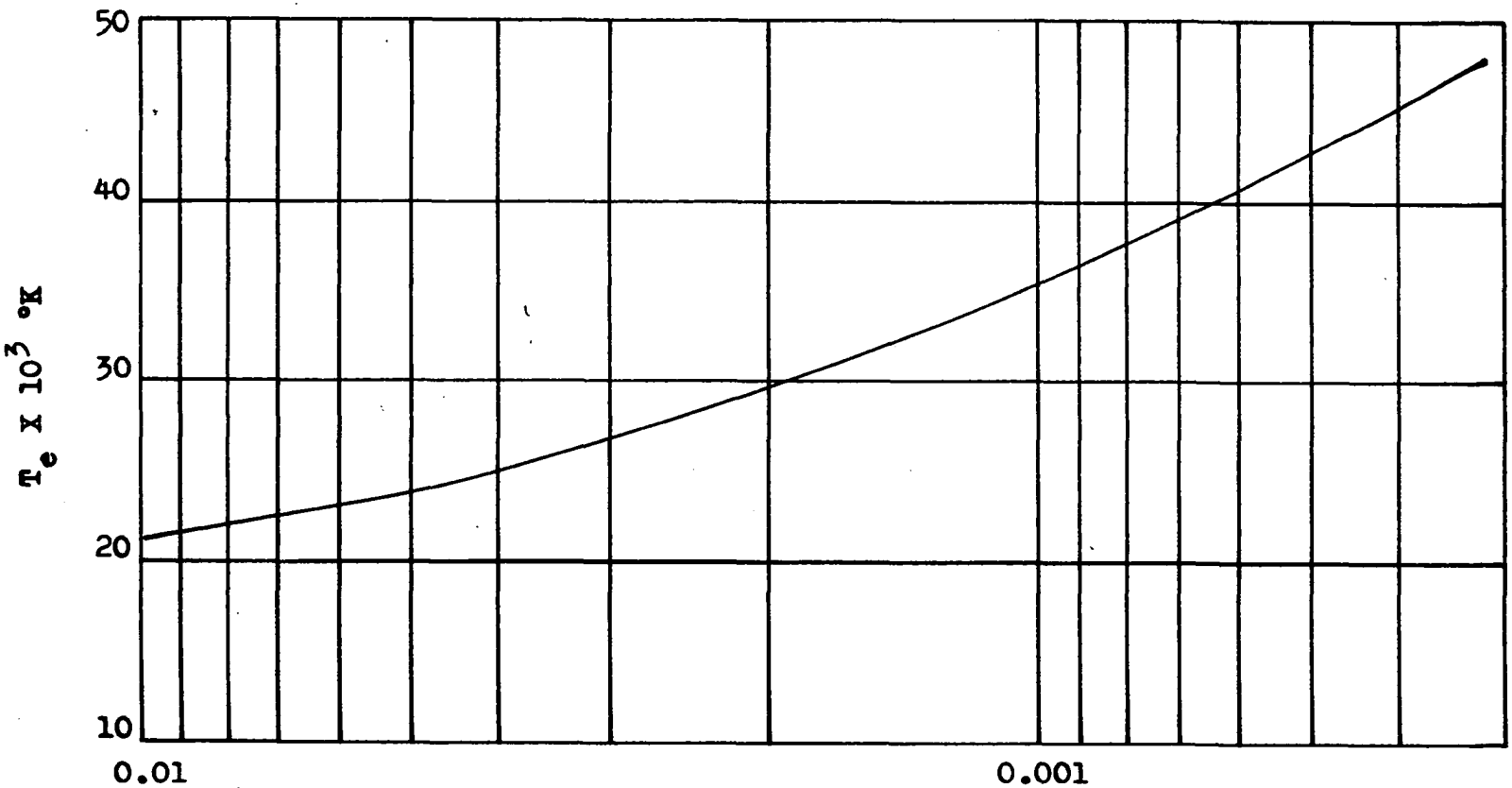


Figure II-5

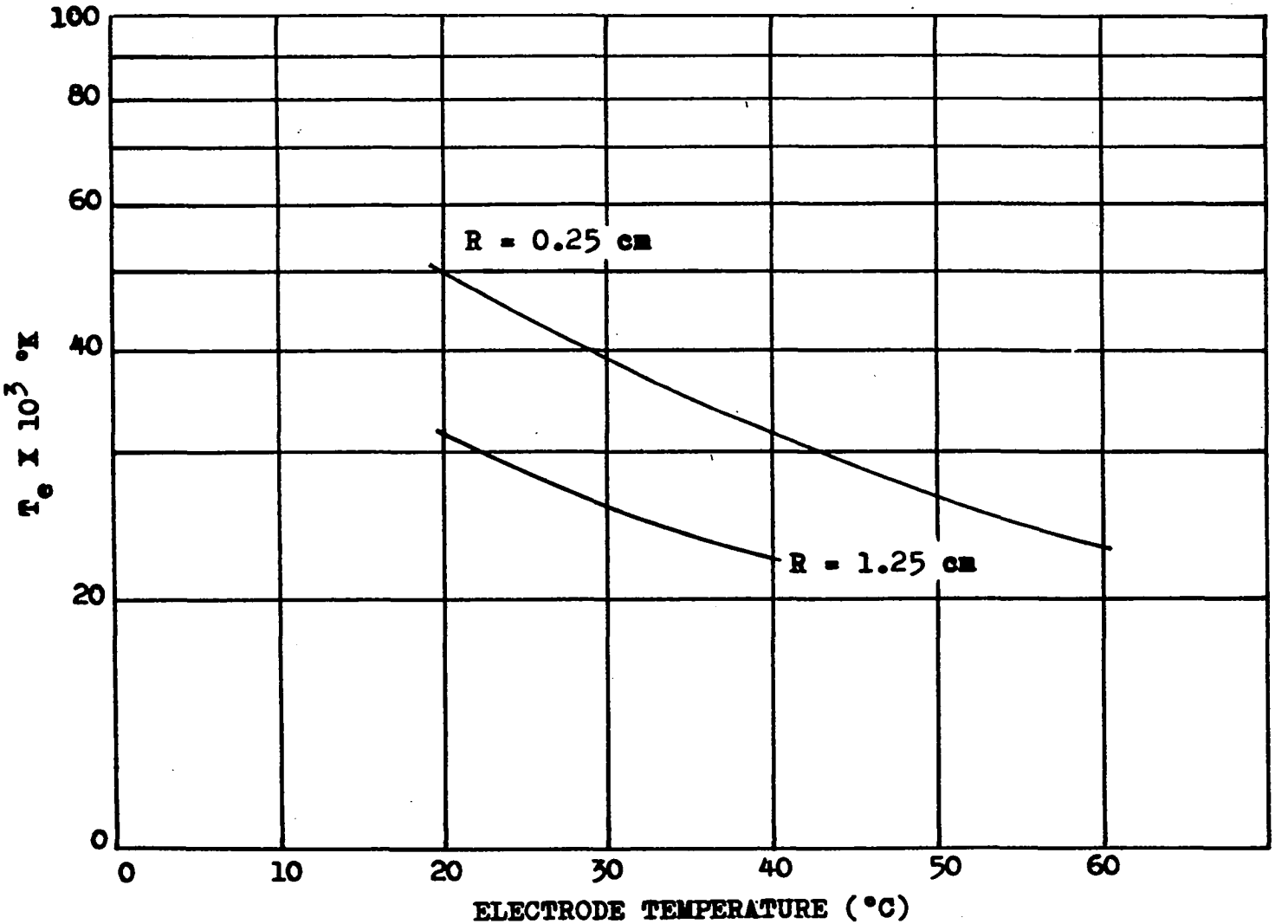

100
80
60
40
20
0
T_e X 10^3 °K
R = 0.25 cm
R = 1.25 cm
0
10
20
30
40
50
60
ELECTRODE TEMPERATURE (°C)

Figure II-6

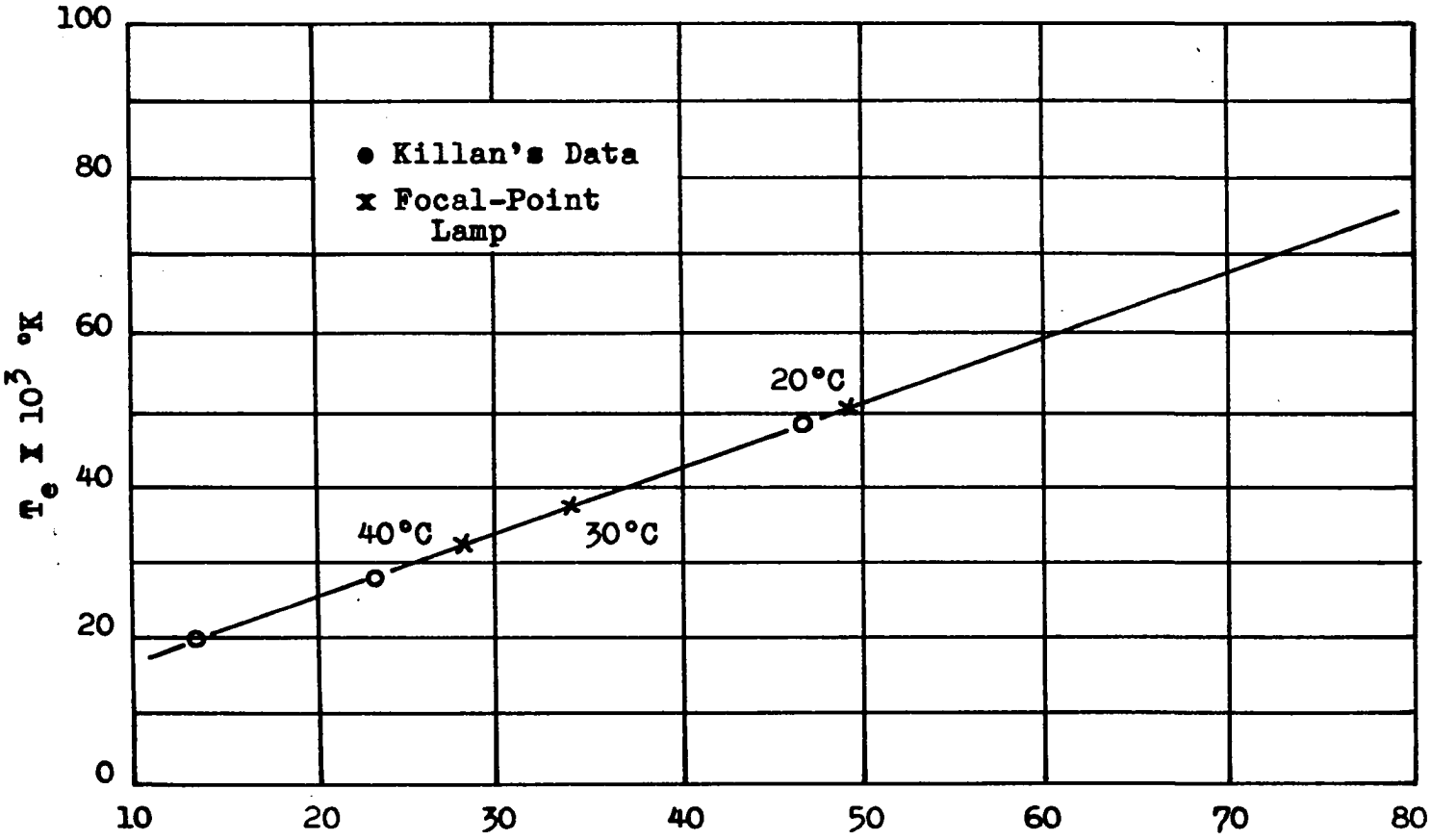

100
80
60
40
20
0
T_e X 10^3 °K
• Killan's Data
x Focal-Point Lamp
20°C
40°C
30°C
10
20
30
40
50
60
70
80
PERCENT ENERGY TO WALLS

Figure II-7

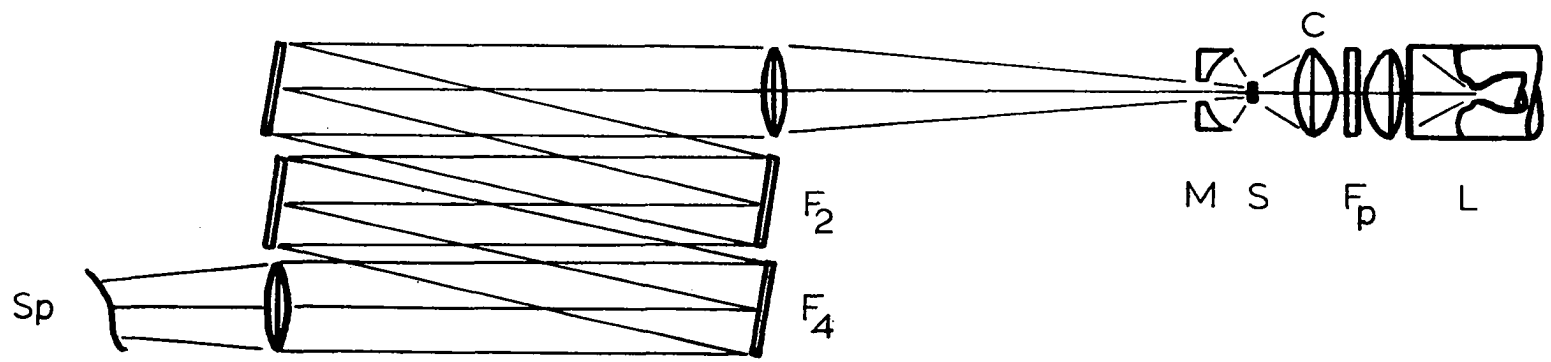
of heat transfer at the constriction in terms of electrode temperatures can be obtained. Killan's data and the focal-point lamp temperatures are plotted in Fig. II-7. These figures for wall-heating are not meant to be taken literally, but to give a qualitative picture. Neglecting any ionization heating effects it can be observed from this curve that an appreciable change in wall heating occurs between 20 and 40°C electrode temperature.

Hence, at low electrode temperatures and correspondingly low Hg-vapor pressures excessive wall heating occurs due to both increasing electron temperature and to ionization occurring at the constriction. It has been established that pyrex glass is not reliably stable to high intensity electron beams. This appears to be a thermal effect due to spot heating; the localized high temperature produced causing strains and consequent cracking.[39] Hence operating the lamp at electrode temperatures of 30°C or higher tends to reduce heating at the constriction with a resultant decrease in strains.

Illumination System

A crystal powder Raman illumination system using the focal-point Hg-lamp, has been constructed as shown schematically in Fig. II-8. An asymmetrical rare-earth glass condenser lens, f/0.58, is located in front of the window with its focal point located at the constriction. A second condenser lens focusses the luminosity of the constricted region on the back of the sample tablet. An interference filter or a chemical filter may be placed between the condenser lenses.

Both interference filters and chemical filters have been used to isolate the 4358 A Hg-line. Interference filters have been purchased



C: Condenser Lens
F_p: Primary Isolation Filter
$F_{1,2,3,4}$: Secondary Rejection Filters
L: Focal-Point, Hg-Lamp
M: Mirror
S: Sample

RAMAN IRRADIATION SYSTEM FOR CRYSTALLINE POWDERS

Figure II-8

from both Baird Atomic, Inc., Cambridge, Massachusetts and Thin Film Products, Inc., Cambridge, Massachusetts. The filters produced by Thin Film Products possess a higher peak transmission for the same bandpass. The interference filter is far superior to chemical filters for eliminating both the continuum and unwanted Hg-lines. The primary interference filter (2 inch by 2 inch) was made on special order by Thin Films Products, Inc. The filter transmits 70% of the Hg-4358 A line with a total bandwidth of 30 A at the half-power point. Using this filter exposures with no sample have been made up to 12 hours and the continuum associated with the Hg-spectrum was not recorded on the film.

The first primary interference filter (Thin Films, Inc.) was found to have shifted its peak of transmission from 4358 A to 4398 A after approximately 1500 hours use. The system was operated continuously over this period and the filter and sample holder were found to have reached temperatures up to 45°C. It is felt that heating affected the cryolite spacers used in the interference filter, causing the transmission peak to shift.[43] For this reason a water-cooled copper filter holder was constructed which allows the filter to be maintained at approximately 25°C. The sample cavity was also fitted with an air-blower to facilitate cooling. The second primary interference filter (Thin Films, Inc.) has not been in use for a sufficient period to determine whether this will be an adequate solution.

The sample tablet is mounted in the apex of a polished aluminum cone such that only radiation from the condenser lens, interference filter system reaches the sample. A 65 mm diameter, f/.325, front

surfaced aluminized Cassegrainian mirror is located behind the sample such that any scattered radiation outside the useful cone of aperture of the spectrograph is refocussed back on the sample.

A 54 mm diameter, f/4.7, coated achromatic lens collimates the radiation from the sample. The collimated light is reflected from four interference filters peaked to transmit 4358 A at 3° incidence with a bandpass of 30 A and reflect all other visible wavelengths. Three of the interference filters were made by Baird-Atomic and transmit 40% of Hg-4358 A, while the fourth filter was made by Thin Film Products and transmits 70% of Hg-4358 A. Theoretically 93% of the 4358 A radiation is eliminated, while the Raman radiation is totally reflected. The radiation is then focussed by a 54 mm diameter, f/6.3, coated achromatic lens on the slit of an Applied Research 3 glass-prism spectrograph with a f/3.5 Matsukov camera.

Sample Thickness

In using a back-illuminated sample, there is a theoretical optimum thickness given by $d_{opt} = 1/k$, where k is the extinction coefficient. For this optimum thickness the intensity of exciting radiation and Raman radiation emerging from the front of the sample should be approximately equal.[27] To test this hypothesis samples of powdered naphthalene were prepared of various thicknesses and k was measured. For the powdered naphthalene d_{opt} was found to be approximately 5 mm. Five minutes exposures with no primary filter were made and developed simultaneously of naphthalene sample tablets with thicknesses of 2, 3, 4, 5, 6, 7, 9 and 11 mm. A portion of the spectrum showing the 1380, 1443, and 1463 cm^{-1} Raman bands and a mercury line are shown in Fig. II-9.

RAMAN BAND vs Hg LINE INTENSITY

$C_{10}H_8$

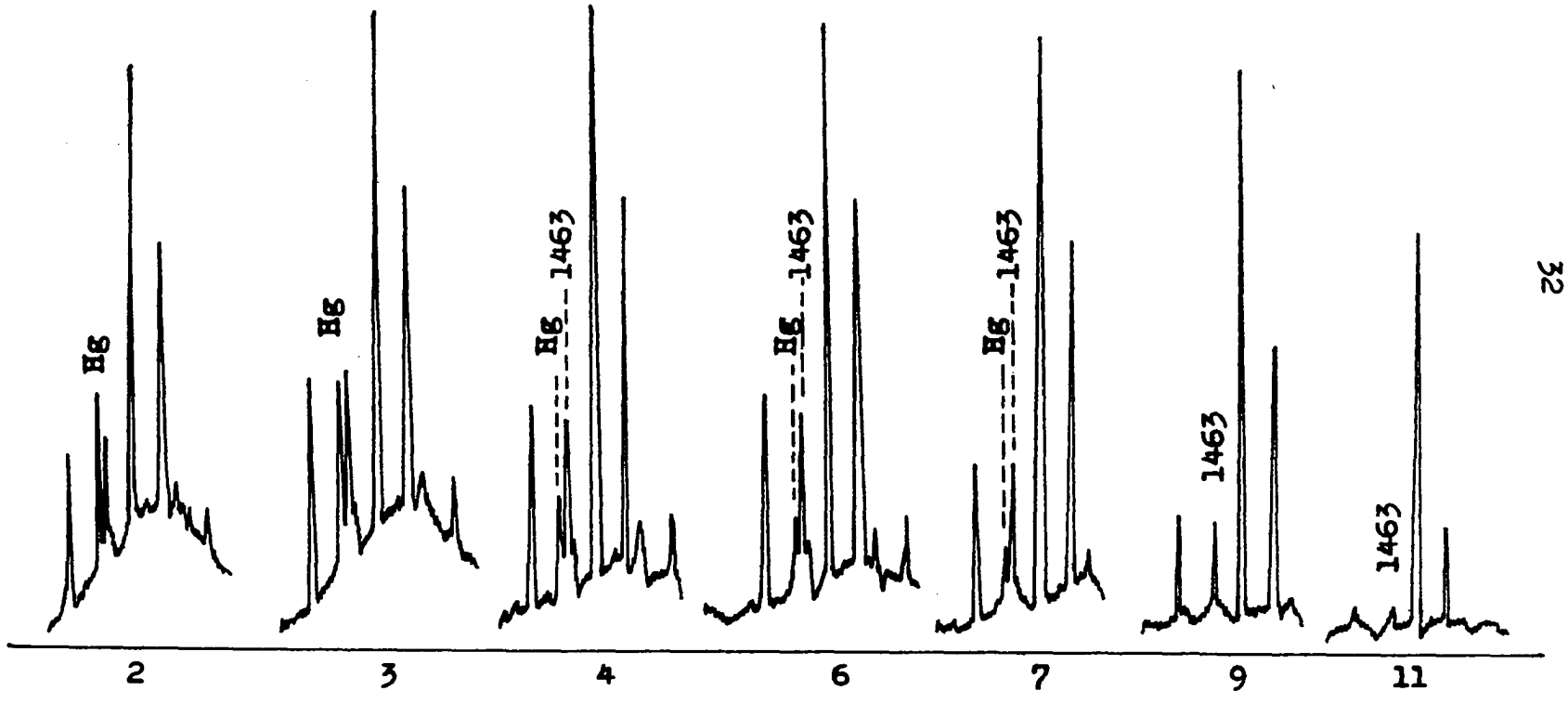


Figure II-9

As is evident from these curves, the optimum Raman band to Hg-line intensity occurs for approximately d = 5 mm. Twenty minute exposures with the primary filter were made and developed simultaneously of naphthalene sample tablets with thicknesses of 2, 3, 4, 5, 6, 7, 9, and 11 mm. The intensity of the 512 and 724 cm^{-1} Raman bands are plotted as a function of sample thickness in Fig. II-10. The maximum intensity was found to occur for a sample thickness of approximately 5 mm. Similar studies on Teflon tablets showed also that $d \doteq 1/k$ yields the best results.

In the preparation of any Raman sample k is measured and the tablet thickness is set equal to 1/k. The apparent measured value of k for a powdered crystalline material depends not only upon the material but also the crystal size composing the powder. The value of k for naphthalene could be changed slightly by variation of the crystal size. The Raman spectrum was found to be slightly more intense for equal time exposures for the smaller value of k providing d_{opt} was used in both cases. It appears that for a given sample, the larger the crystals, then the larger d_{opt} will be and the more intense will be the Raman spectrum provided one uses 1/k for the sample thickness. For Teflon d_{opt} was equal to 2 mm, while for the finer-powdered long-methylene chain compounds d_{opt} was of the order of 0.5 mm or less. Sample thicknesses of less than 0.5 mm have not given good Raman spectra.

Film and Developer

Commonly Eastman Kodak Royal X-Pan and Tri-X Pan are used as Raman films due to their speed and grain characteristics. However, if photographic glass plates can be used, then the high speed, long-exposure

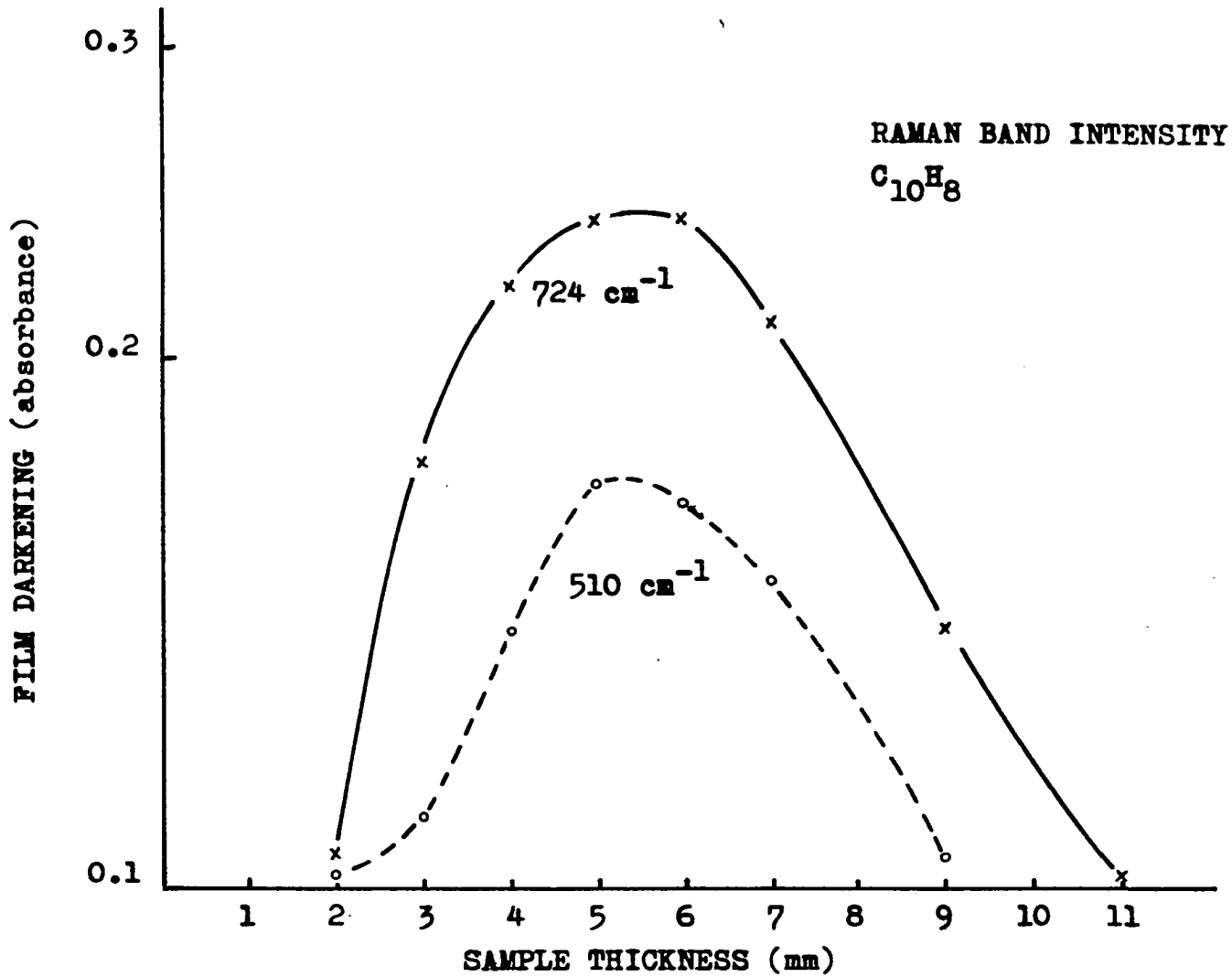

RAMAN BAND INTENSITY
$C_{10}H_8$
724 cm^{-1}
510 cm^{-1}
FILM DARKENING (absorbance)
0.3
0.2
0.1
1
2
3
4
5
6
7
8
9
10
11
SAMPLE THICKNESS (mm)

Figure II-10

characteristics of the EK-103a-O emulsion is the better choice. The 103a-O emulsion is intended to be used for exposures involving weak sources of light and long times such as occur in astronomy or Raman spectroscopy.

A comparison was made between Royal-X Pan film and 103a-O plates with a Raman sample of naphthalene and the Hilger E612 spectrograph with f/5.6 camera. The superiority of the 103a-O plate lead to a special order of 103a-O emulsion placed on a 35 mm polyester base to be used with the Applied Research f/3.5 spectrograph. A comparison between the 103a-O emulsion as supplied on a glass plate and on the polyester base showed the plate to be faster by a factor of approximately 2. A measurement of the weight of the emulsion per unit area on the plate and the film showed the plate emulsion to be heavier by a factor of 1.6. This may account for the difference in speed.

Because of the recent appearence of new film developers with high acutance and the claim that such developers could increase the speed of the 103a-O emulsion,[45] tests were made to determine the best developer. Both Acufine and Diafine (Baumann Photo Chemicals, Chicago, Illinois) were used and compared to the recommended Eastman Kodak D-19. The tests were made on equal time exposures of powdered naphthalene. While the high acutance developers seemed to enhance the stronger Raman bands, the general background was increased to the detriment of weaker Raman bands. It was concluded that D-19 developer applied for 8 minutes at 20°C gave the best results for the 103a-O emulsion.

Performance

It is difficult to compare speed and efficiency between Raman

illumination systems. For solid samples, densitometer tracings of the actual exposures and data on background are seldom reported. In making a comparison the author feels that the ultimate speed is not necessarily the best criterion. Both the speed and ultimate sensitivity must be judged together. While Tobin's system is undoubtedly fast, it is severely limited in ultimate sensitivity by a relatively high background. The focal-point Hg-lamp, back-illuminated sample system is slightly slower than Tobin's system but is not sensitivity-limited by the background.

In recent years the Raman spectrum of powdered naphthalene has been used as a standard of comparison between various systems. Moser and Stieler[27] reported 35 vibrational Raman bands for naphthalene between 400 and 3300 cm^{-1}. They did not indicate the sample thickness nor length of exposure. Using the previously described system the author has recorded some 52 Raman bands in the 400 cm^{-1} to 3300^{-1} region for powdered naphthalene. These bands are tabulated in Table II-1. A densitometer tracing of the 400 to 1600 cm^{-1} region of a four hour exposure of a 5 mm thickness naphthalene sample is shown in Fig. II-11. The background is due to a slight fluorescence in pure naphthalene.[46] This tracing is far superior to any reported by Moser and Stieler.

Ferrano, et al.,[47] using a Cary Model 81 Raman Spectrograph which has an illumination system similar to that shown in Fig. I-1 with a thirteen-helical coil, Toronto Hg-lamp have reported that they observed only 20 Raman bands for naphthalene.

To test the exciting line rejection system an iron-arc was mounted at the sample position and several exposures were made. Examination of the

TABLE II-1

RAMAN DATA - POWDERED NAPHTHALENE

This Study	Moser and Stieler
Wavenumber in cm^{-1}	
377 m[a]	406 vw
453 vw	433 w
464 vw	464 m
489 vvw	483 vw
510 vs	512 vs
660 vw	
706 w	708
724 m	725 m
762 vs	765 vs
781 m	784 m
949 w	952 w
962 (1022f)[b] w	
979 w	980 w
1023 vs	1022 vs
1090 (1147f)[b] vw	
1147 s	1150 s
1159 w	
1167 ms	1168 s
	1205 vw
1243 m	1243 ms
1259 vvvw	1259 vw

TABLE II-1 (Continued)

This Study	Moser and Stieler
Wavenumber in cm^{-1}	
1278 m	1278
1323 (1380f)[c] s	1323 m
1336 w	1338
1380 vvs	1383 vvs
1406 (1463f)[b] w	
1443 s	1446 s
1463 vs	1465 vs
1490 vw	1494
1520 (1575f)[b] w	
1539 w	1527 w
1575 vs	1578 vs
1593 w	1599 vw
1626 m	1629 m
2277 vvw	
2403 vvw	
2503 vw	
2563 vw	
2711 w	
2755 w	
2862 w	
2901 w	
2949 (3002f)[c] m	

TABLE II-1 (Concluded)

This Study	Moser and Stieler
Wavenumber in cm^{-1}	
2973 m	
3002 vs	3007
3017 m	3019
3029 m	3032
3055 vvs	3055
3149 w	
3183 w	
3210 vw	
3250 m	3245

(a) Intensity was estimated visually from a photographic plate. The abbreviations v, s, w, m mean very, strong, weak, and medium respectively.

(b) Raman band excited probably by Hg-f (4313 A).

(c) Raman band excited probably by Hg-f, but intensity indicates a new Raman band also.

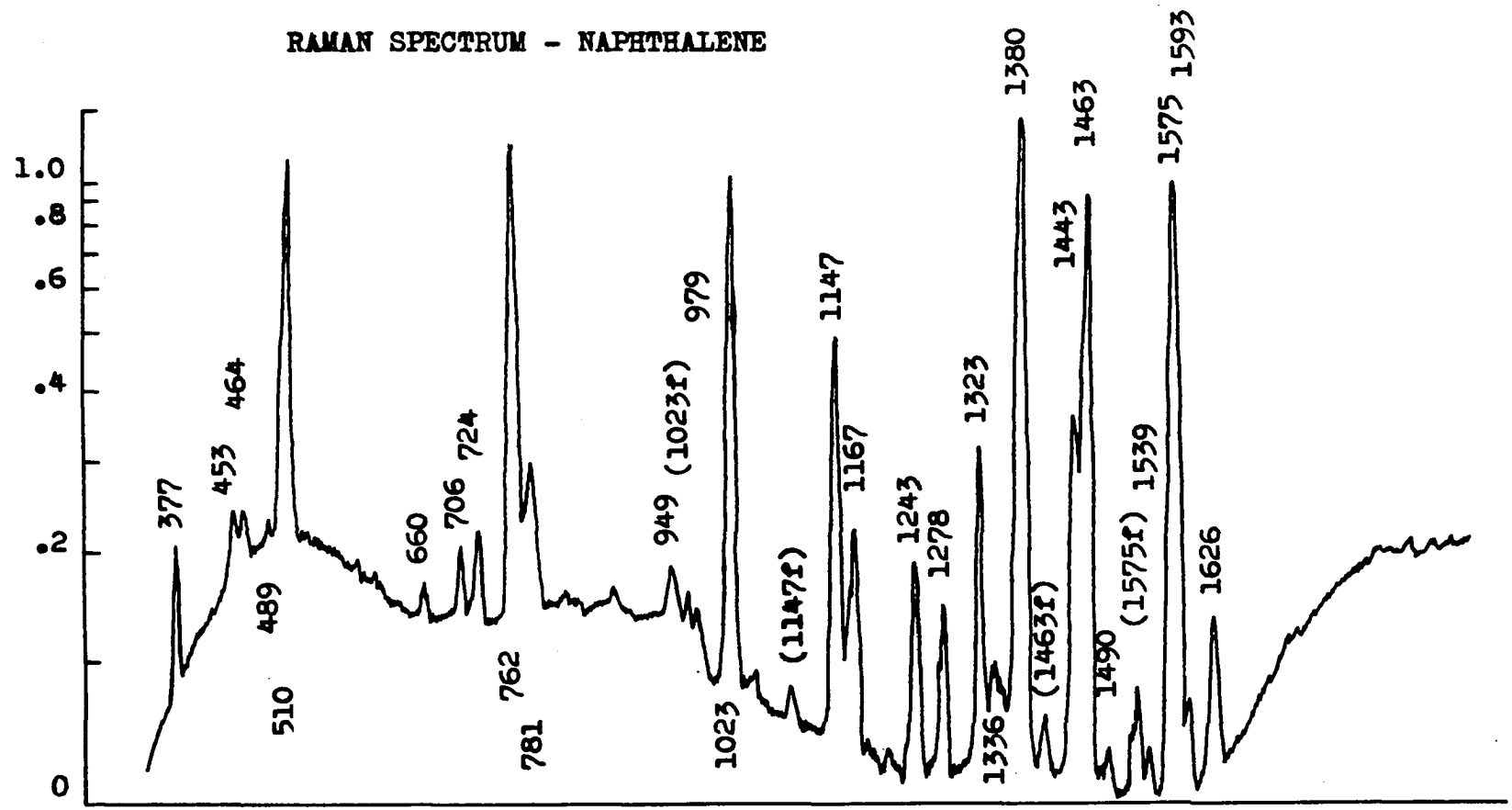

RAMAN SPECTRUM - NAPHTHALENE
1.0
.8
.6
.4
.2
0
377
453
464
489
510
660
706
724
762
781
949
(1023f)
979
1023
(1147f)
1147
1167
1243
1278
1323
1336
1380
(1463f)
1443
1463
1490
(1575f)
1539
1575
1593
1626

Figure II-11

spectra showed that all radiation $\pm$ 100 cm^{-1} on either side of the 4358 A line was effectively removed. Several exposures were made also with a continuous tungsten lamp source in the Hg-lamp position. Examination of these spectra showed some modulated background in the 100 to 200 cm^{-1} region. This is caused probably by the overlapping of the finite bandwidths of the primary interference filter and the four rejection filters. The primary filter used to isolate the Hg-4358 A line also passed weakly several unwanted Hg-lines in the 100 to 200 cm^{-1} region. Because of these observations, it was not found feasible to measure Raman bands below 200 cm^{-1}. With naphthalene as a sample, however, the 118 cm^{-1} Raman lattice vibration band was recorded. Without using a rejection filter system, Moser and Stieler were able to record Raman bands as low as 13 cm^{-1}.

Raman spectra as good as those obtained by Nielsen and Woollett[25] of normal paraffins and polyethylenes in exposures as long as 100 hours were obtained with exposure times ranging from 4 to 24 hours. Tobin was able to obtain such data in as little as 3 hours, but added no new information. Woollett and Nielsen[25] reported 13 Raman bands of the normal paraffin n-C_{36} H_{74} with a 108 hour exposure. The author has found 22 Raman bands of the same sample using exposure times up to 72 hours. These bands are tabulated in Table II-2. Figure II-12 shows a densitometer tracing of the Raman spectrum obtained by Nielsen and Woollett and by the author. The high background in the 12 hour exposure on n-C_{36} obtained by the author was due to sample fluorescence. The sample used was the same as used by Woollett and had become highly fluorescent over a period of years. A better sample was obtained from Phillips Petroleum at

TABLE II-2

RAMAN BANDS - $n\text{-}C_{36}H_{74}$ CRYSTALLINE POWDER

This Study	Nielsen and Woollett
Wavenumber in cm^{-1}	
2965 w	2966 w
2931 w	2936 w
2903 w	
2882 vvs	2884 vvs
2848 vvs	2850 vs
2784 w	
2721 w	2721 w
1463 s	1466 w
1440 s	1441 m
1415 s	1418 m
1372 m	
1295 vs	1294 s
1268 vvw	
1238 vvw (1295f ?)	
1170 w	1171 vw
1132 m	1133 m
1113 vvvw	
1062 m	1063 m
1003 vvvw	
956 vvvvw (?)	
891 w	890 vw
841 vvvw	
808 vvvw	

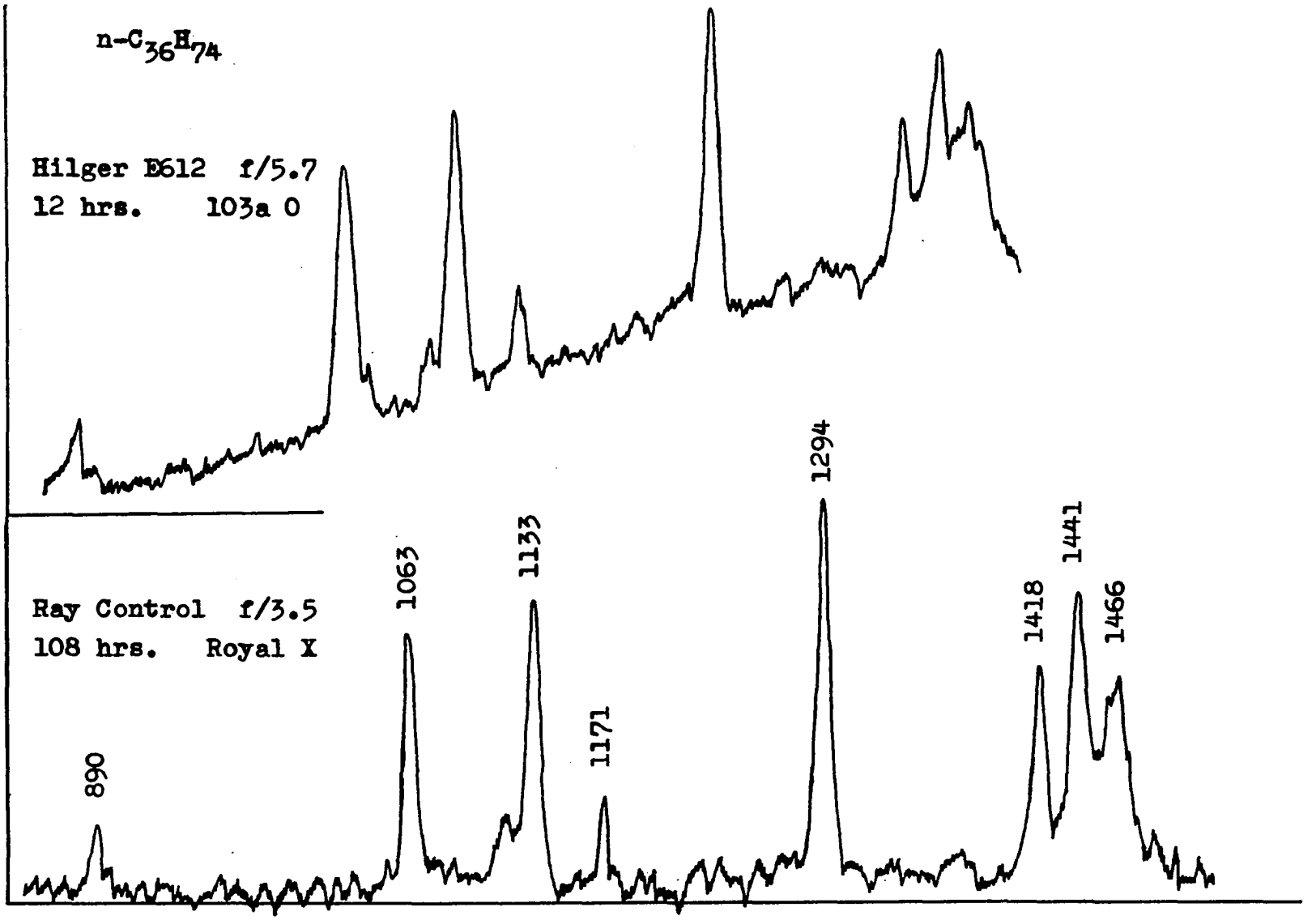

n-C36H74
Hilger E612 f/5.7
12 hrs. 103a 0
Ray Control f/3.5
108 hrs. Royal X
890
1063
1133
1171
1294
1418
1441
1466

Figure II-12

a later date for the 72 hour exposure. Although good samples of crystalline polyethylene have been prepared, an extensive Raman study has not been made.

Several authors[7,48] have made an effort to obtain the Raman spectrum of the polymer polytetrafluoroethylene (Teflon), but have failed. The Raman spectrum of a commercial Teflon sample, 2 mm in thickness, was obtained by the author[49] in a 15 hour exposure using the Hilger E612 spectrograph with f/5.6 camera. Exposures up to 72 hours yielded no new information. A rudimentary spectrum of the powdered polymer polyvinyl chloride has been obtained in a 12 hour exposure but will not be reported pending further work.

An extensive Raman study has been made of powdered crystalline samples of normal dibasic carboxylic acids and will be reported in Part II of this dissertation. Raman exposures of 72 hours were made. Recently Anathanarayanan[17] has reported the Raman spectrum of single crystals of two of these acids with 72 hour exposures using the Hg-2537 A line. Comparison with his spectra show results obtained by the author to be at least as good above 200 cm^{-1}. Below 200 cm^{-1} the Hg-2537 A system is superior due to the ease with which the 2537 A line can be eliminated.

For excitation of Raman scattering in crystalline powders and polymers the focal-point Hg-lamp system appears to be superior to other systems reported.[26,47] The usefulness of the system for clear solid samples and liquids is doubtful because of the requirement that $d_{opt} = 1/k$. Attempts to obtain Raman data on carbon tetrachloride in a cell placed immediately behind the primary interference filter were not fruitful. It is doubtful that optimum results can be obtained with the

same illumination system for liquids and crystalline powders, contrary to the desire of various authors.[26,47] This is not surprising due to the totally different characters of these two states.

CHAPTER III

POSSIBLE IMPROVEMENTS IN THE RAMAN SPECTROSCOPY OF SOLIDS

Focal-Point Raman Illumination System

Several improvements of the present system could be made. The necessity of eliminating the exciting line prior to its entry into the spectrograph requires the use of the rejection interference filter system which causes problems in making Raman measurements below 200 cm^{-1}. Furthermore, the present rejection system requires reflection from four filters with an optical path of 2.5 meters. This makes alignment of the system difficult. With the improvement in available interference filters, a rejection system using two filters transmitting 70% of Hg-4358 A could be constructed which would eliminate 91% of the exciting line and would make alignment easier. Additionally, an optical arrangement using two-right angle prisms in a positive-look system could be constructed such that the rejection filter system could be by-passed without realignment of the system. This would facilitate obtaining information on Raman shifts in the 0 to 200 cm^{-1} region.

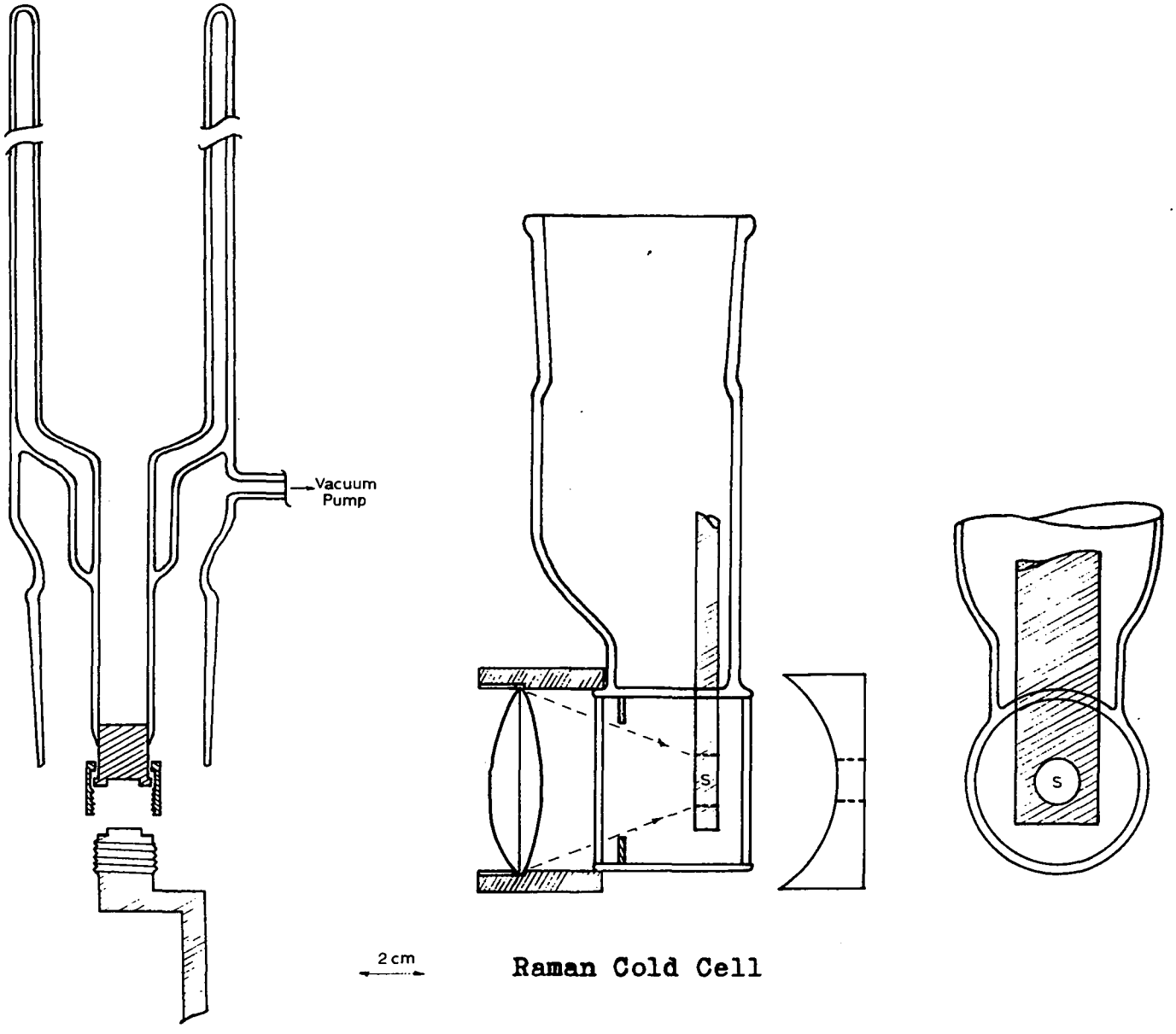
Because the sample is located close to the Hg-lamp, sample heating is a problem. It was not found feasible to make 72 hour data runs on samples whose melting points are below 35°C. It is often desirable to obtain Raman data on solids whose melting points are below room

temperature[50,51] and on certain crystals at liquid nitrogen and helium temperatures.[52,53] For these reasons a dewar system has been constructed as shown in Fig. III-1 which should allow Raman data to be obtained on samples at temperatures down to 77°K. This system has not yet been tested.

Only the Hg-4358 A line of the focal-point Hg-lamp has been used to excite Raman scattering in the present study. Because interference filters with high peak transmission are not available in the 4000 A region Hg-4047 A was not used. However, it may be possible to use the Hg-5461 A line to excite Raman scattering in samples which absorb in the 4000-5000 A region. While this line is not as intense as the 4358 A line normally, it may be possible to enhance the intensity of Hg-5461 A line by the admixture of a small amount of nitrogen gas.[54] An investigation of foreign gases introduced into this lamp and the resultant affect on the Hg-line intensity could prove fruitful.

Laser Raman Excitation

Several papers[21,22,23,24] have reported the use of a laser as a Raman excitation source. The results thus far have not surpassed the data obtained with Hg-lamps for equal time exposures. The best choice for laser Raman excitation is apparently the continuous wave, Neon-Helium 6328 A laser line. The probability of Raman scattering at 6328 A is less than that at 4358 A by a factor of approximately five. Furthermore it has been calculated that a 2.5 KW Toronto mercury arc radiates approximately twice the power in the 4358 A line to the sample than a 400 mw laser.[24] Hence the Hg-lamp appears to be superior at the moment for Raman excitation in the visible region. However, the perfection



Raman Cold Cell

Figure III

of an ionized-argon laser radiating 10 watts continuously in a single line in the blue-green portion of the spectrum[55,56] could easily replace the Hg-lamp.

The laser as a source of Raman excitation in the red and near-infrared regions of the spectrum is probably far superior to the He-arc lamps commonly used. The use of the 6328 A and 1.15 μ lines of the cw Ne-He laser should allow Raman study of a number of crystals which cannot be studied with visible excitation because of absorption. Paramagnetic ion-doped crystals, semiconductor crystals, superconductor crystals, and piezo-electric crystals are examples of crystals which frequently absorb in the visible region and hence have not been studied with the Raman effect. Several theoretical papers[12,57,58] have been written on the Raman effect in such crystals, but little experimental work[52] has been done. With a laser as an excitation source, these crystals could be studied with the Raman effect. For such a Raman illumination system based on a line in the near infrared the use of the Fourier transform spectroscopic technique[59] should yield an appreciable gain. The low number of spectral elements involved in Raman spectra makes it particularly applicable to this technique.

PART II: VIBRATIONAL SPECTRA OF NORMAL DIBASIC CARBOXYLIC ACIDS

CHAPTER IV

PREVIOUS WORK ON CRYSTAL STRUCTURE AND VIBRATIONAL SPECTRA OF NORMAL DIBASIC ACIDS

Introduction

Homologous series of compounds with long methylene chains are capable of crystallizing in a variety of crystal structures. Moreover, any given compound with a particular chain length usually can crystallize in one of several polymorphic forms. The vibrational spectra of crystals of such compounds are characterized by certain frequencies associated with methylene chain vibrations and other frequencies associated with end group vibrations. The observed frequencies can not always be so simply characterized, since chain and end group vibrations of similar frequency and of the same species interact or mix. The determination of the frequencies associated with the methylene chain and end group vibrations of various long methylene chain compounds has been the subject of numerous papers. Holland[60] has given an excellent review and bibliography of such investigations up to 1961.

The dichroism of the vibrational bands of single crystals of compounds with long methylene chains is determined by the molecular

structure and the crystal form. The polarized infrared spectrum of a given long chain compound in the crystalline state has been shown to be very sensitive to the crystal structure and has been useful in determining new crystal forms.[61] In recent years the dichroism of single crystal forms of the long-chain normal paraffins, $CH_3(CH_2)_nCH_3$, and the related normal monobasic carboxylic, or fatty acids, $CH_3(CH_2)_nCOOH$, have been the subject of investigations in this laboratory.[60,61,62,63,64] The compounds studied have been true long-chain molecules, the shortest chain possessing fourteen methylene groups.

The vibrations of crystals with very long methylene chains have certain simplifying features. In the crystalline phase only the extended chain conformation is present, and the vibrational problem is similar to that of a linear chain of coupled harmonic oscillators. The longer the methylene chain, the less is the influence of the end groups, and the more nearly does the vibrational problem approach that of an extended infinite polymethylene chain. The chain vibrations may be classed in sets, each set being associated with a characteristic motion of a methylene group. If the chain contains N methylene groups, there will be approximately N vibrations in each set. For large N, the frequency distribution and frequency range should be independent of N. Recent calculations on normal paraffins by Snyder[65,66,67] have been able to account not only for the frequencies but also for the infrared absorption intensities associated with these methylene motions. Snyder has also shown that, even for large values of N, the overlapping of these methylene vibrational sets causes a mixing of the simple motions. In particular, the bands associated with the rocking and twisting motions

of the methylene groups cannot be clearly separated. It is more correct to characterize these bands as rocking-twisting or twisting-rocking motions, depending on which motion is dominant, rather than ascribe them to either rocking or twisting.

The crystalline state of shorter chain length compounds has not been extensively investigated. Generally the melting points of such compounds are below room temperature, making such a study impractical. However, an investigation of a series of shorter chain length compounds should yield information on the development of sets of methylene vibrations and the effect of the end groups upon these vibrations. The normal dibasic carboxylic acids, $HOOC(CH_2)_nCOOH$, form a homologous series whose members, for all values of n, exist in the crystalline phase at room temperature.

A vibrational study of this series of acids for n = 1, 2, 3, 4, 5, 6, 7, 8 and 12 has been made by the author. Both Raman and polarized infrared absorption data have been obtained. These data will be presented and interpreted with the help of the known molecular and crystal structures and will be related to similar data for n-paraffins and n-fatty acids.

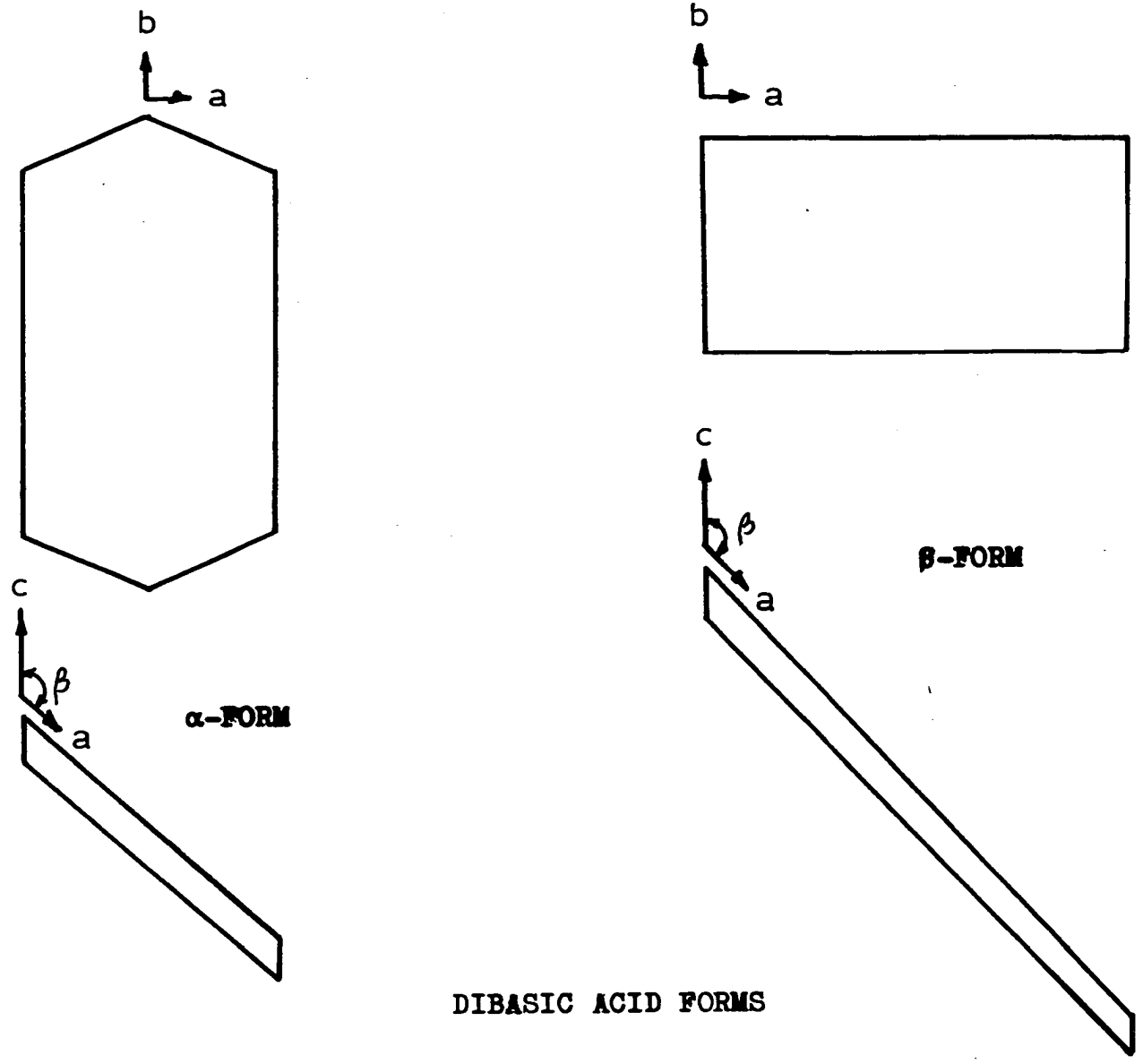
Crystal Structure

A normal dibasic carboxylic acid, $HOOC(CH_2)_nCOOH$, consists of n methylene groups, in the crystalline state, having a nearly planar zig-zag carbon skeleton and at each end a carboxyl group which does not generally lie in the skeletal plane. Very strong hydrogen bridges form between the carbonyl and hydroxyl groups of adjacent molecules, causing the association, end to end, of many chains. This association persists to some extent even in the vapor state, and the abnormally strong hydrogen

bonding causes vibrations associated with the carboxyl group to be distorted from the normal.

Caspari[67,68] studied the structure of single crystals of dibasic acids with 4, 5, 6, 7, 8, 11 and 16 methylene groups by x-ray diffraction. He concluded that the unit cell of acids with an even number of carbon atoms contains two molecules and that the unit cell of acids with an odd number of carbon atoms contains four molecules. For the even acids he found only one form, α, with a space group C_{2h}^5. However, for azelaic acid, $HOOC(CH_2)_7COOH$, he reported two polymorphs, α and β, with space groups C_{2h}^5 and C_{2h}^2, respectively. Both α- and β-forms were found to be monoclinic prismatic crystals. The α-form crystals showed a rhomboidal or six-sided contour, while the β-form crystals had rectangular contours as shown in Fig. IV-1. He reported that they could be distinguished easily by examination under a microscope. No difference in melting points was reported between the two crystal forms, implying that the difference in the lattice energy between the α- and β-form is small. Caspari believed the β-form to be the less stable modification.

Dupré la Tour,[70,71] in the course of a careful investigation of polymorphism in mono- and dicarboxylic acids, determined the cell constants and space groups of a number of the acids in this series. His studies were done on powder samples rather than single crystals, and hence no description of the physical character of the crystal forms was given. He reported two forms, α' and β', for malonic acid ($HOOC(CH_2)_1COOH$), succinic acid ($HOOC(CH_2)_2COOH$), glutaric acid ($HOOC(CH_2)_3COOH$), and pimelic acid ($HOOC(CH_2)_5COOH$). For all of these acids he reported a transformation of the β'- to the α'-form to occur at a temperature somewhat



DIBASIC ACID FORMS

Figure IV-1

below the melting point. He also found two crystal forms for the dicarboxylic acids with 11, 13, 15 and 17 carbon atoms and transitions from the β'- to the α'-form for the acids with 11 and 17 carbon atoms.

Dupré la Tour stated that the α' configuration is the high temperature crystal form. It is apparent, therefore, that Caspari's β-form is the same as la Tour's α'-form. Since much of the present work was based on the identification of the crystal form by microscopic examination, the crystal nomenclature of Caspari will be used.

MacGillavry[72,73,74] and her co-workers have made detailed structural investigations of α-succinic, α-glutaric, α-adipic and α-pimelic acids. Two-dimensional Fourier synthesis studies of α-succinic, α-glutaric, α-adipic and α-sebacic acids have been made by Morrison and Robertson[75,76,77,78] and their co-workers. Recently, Morrison and Robertson [79] have carried out a three-dimensional Fourier analysis of α-succinic acid. From these studies it is evident that Caspari's report of the C_{2h}^5 space group for the odd α-acids is in error and that the odd α-acids have the space group C_{2h}^6. The cell constants and space group of a β-form of azelaic acid grown in this laboratory were determined by Van der Helm.[80] He reports a space group C_{2h}^5 contrary to Caspari's C_{2h}^2.

It has been demonstrated that the crystal forms of oxalic acid, HOOC.COOH, and malonic acid, $HOOC(CH_2)_1COOH$, the first acids in the series, are substantially different from those of the higher carboxylic acids.[81,82] Furthermore, while the carboxyl groups in the higher acids are symetrically arranged, in malonic acid one of the carboxyl groups is turned 13° out of the plane of the methylene carbon atoms, while the

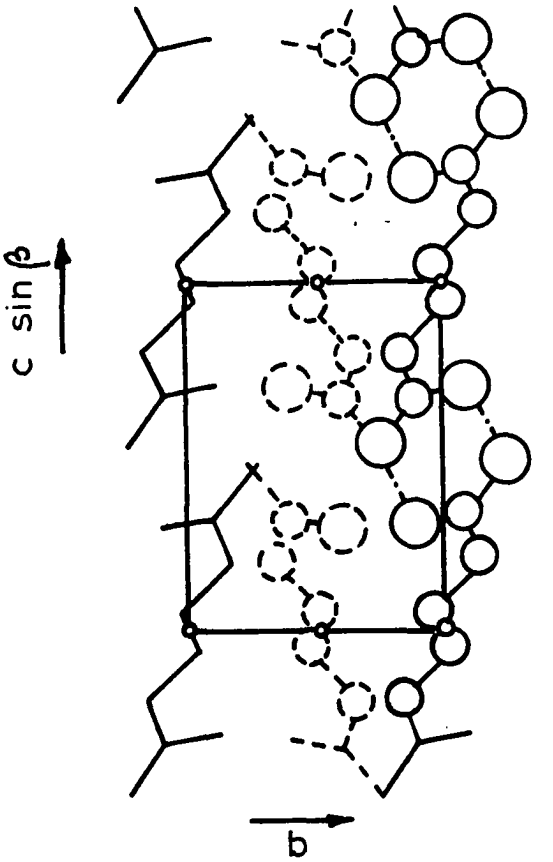
other is nearly at right angle to this plane. For these reasons we shall consider succinic acid to be the first "regular" member of the even-acid series, and glutaric acid to be the first "regular" member of the odd-acid series.

There is some uncertainty in the knowledge of crystal structure of the β-form of the odd acids. No definitive study of this form has been made. The α-form of glutaric and pimelic acids appears well established and the α-form of azelaic acid can probably be predicted from these data. The α-form of pimelic acid is shown in Fig. IV-2. Only one form, the α-form, has been reported and is known with certainty for the even acids. The α-form of adipic acid is shown in Fig. IV-3. A comparison between adipic and pimelic acids is shown in Fig. IV-4.

The crystal structure data on this series of acids is summarized in Table IV-1. N represents the number of molecules per unit cell. The angle β represents the angle between the crystallographic a- and c-axes. The angle θ represents the approximate angle between the plane of the carboxyl end group and the skeletal plane. The temperature, $T_{\alpha \rightarrow \beta}$ represents the transformation temperature from the α- to the β-form. T_m is the melting point.

All crystals of both the regular even and odd series of these acids are monoclinic. Although the space group is different for the even and the odd members, they are built on the same pattern; the molecules are arranged in chains very nearly along the c-axis, with the carboxyl groups of successive molecules joined by two hydrogen bonds. The carboxyl groups are related to one another by a center of symmetry. In the even acids there is a center of symmetry on the central C-C bond,

PROJECTIONS OF α-ADIPIC ACID UNIT CELL



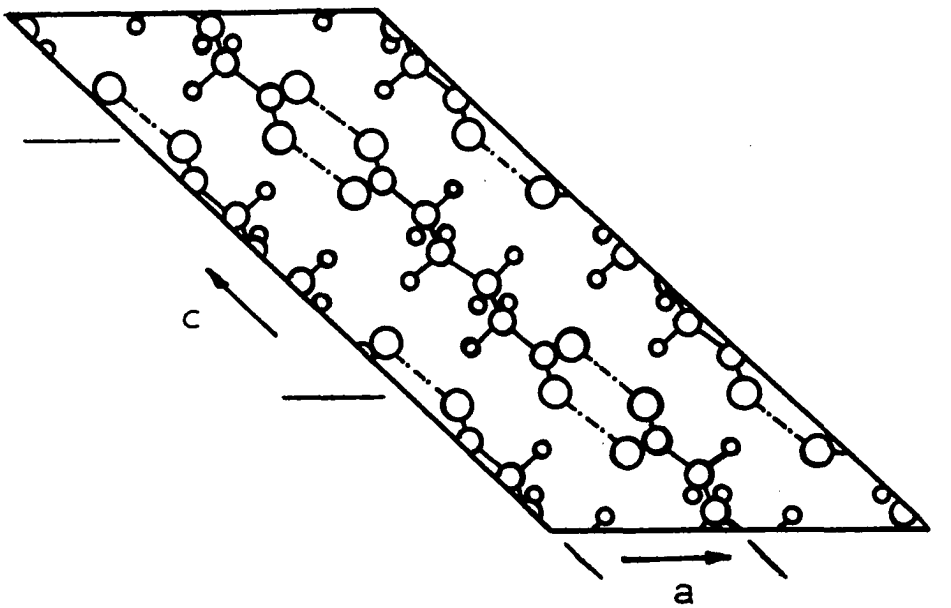


Figure IV-2

PROJECTIONS OF α-PIMELIC ACID UNIT CELL

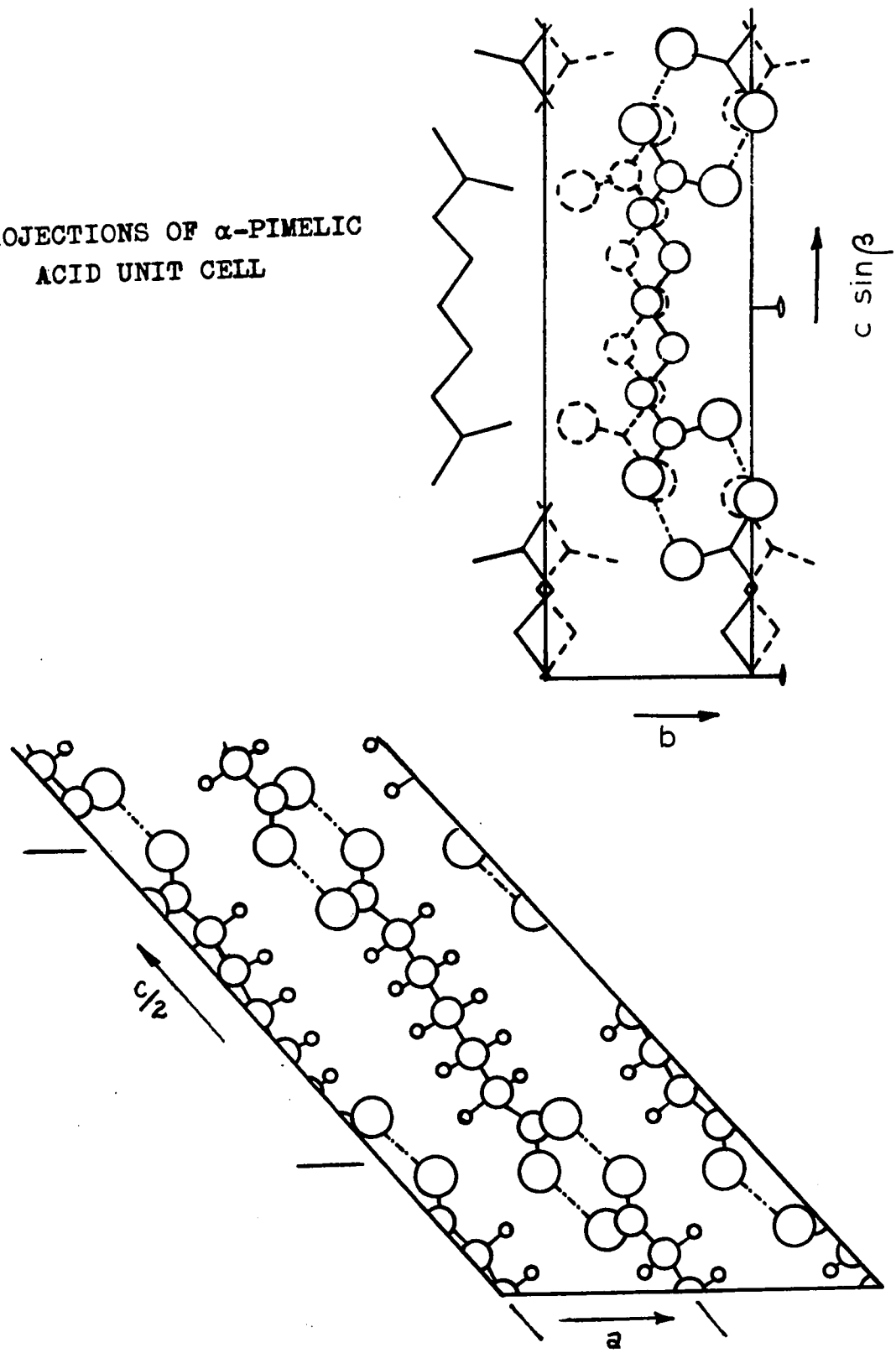
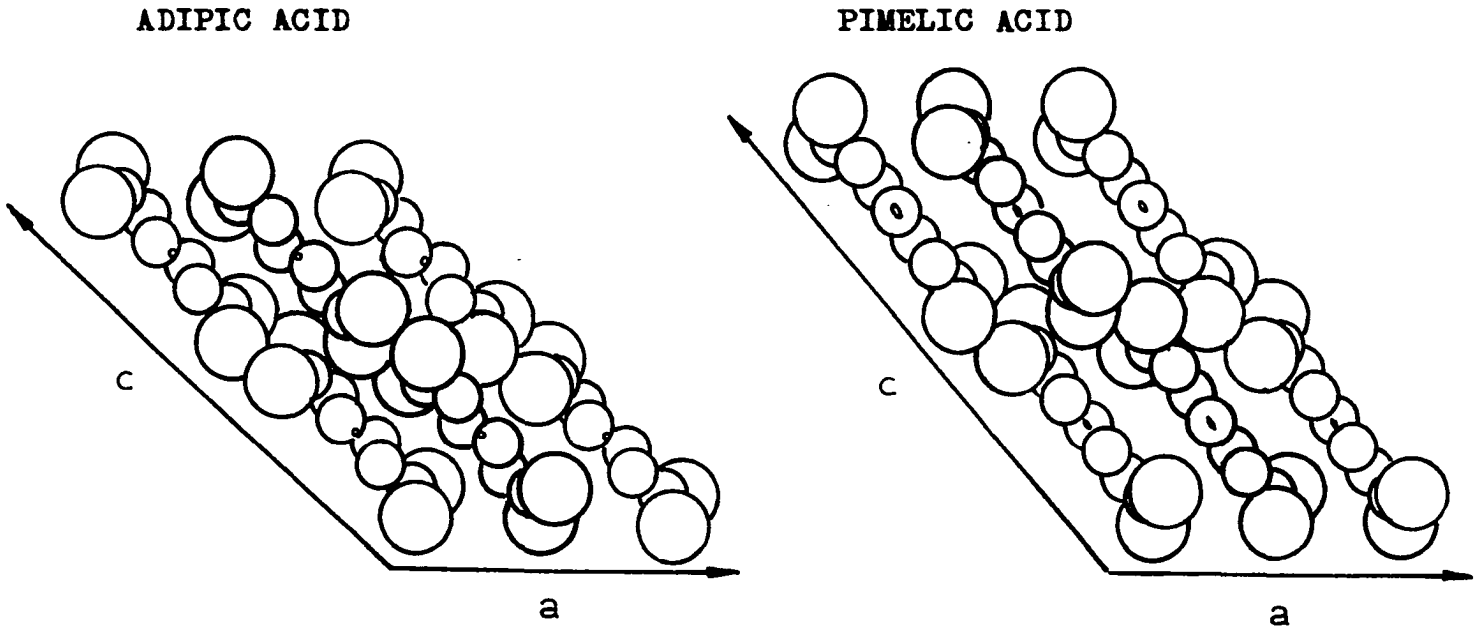


Figure IV-3



COMPARISON OF EVEN AND ODD ACIDS

Figure IV-4

TABLE IV-1

Acid	Cell Constants a	b	c	β	N	Space Group	θ	$T_{\alpha\rightarrow\beta}$ °C	T_m °C	References
Succinic, $C_4H_6O_4$										
α	5.13	8.88	7.62	133°36'	2	C_{2h}^5	11°	137	185	70,75
β	5.70	26.28	7.57	115°45'	-	C_{2h}^3	-			70
Glutaric, $C_5H_8O_4$										
α	10.06	4.87	17.40	132°36'	4	C_{2h}^6	32°	74	97.5	78,70,72
β	10.34	5.08	32.9	129°	8	C_{2h}^6	-			70
Adipic, $C_6H_{10}O_4$										
α	10.07	5.16	10.03	137°05'	2	C_{2h}^5	6°	-	152	76,73
Pimelic, $C_7H_{10}O_4$										
α	9.84	4.89	22.43	130°40'	4	C_{2h}^6	30°	75	103	72
β	22.20	9.59	45.4	137°14'	32	C_{2h}^6				70
Suberic, $C_8H_{14}O_4$										
α	10.12	5.06	12.58	135°00'	2	C_{2h}^5	-		140	68
Azelaic, $C_9H_{16}O_4$										
α	9.72	4.83	27.14	129°30'	4	C_{2h}^2 ?	-		106	68
β	5.62	9.60	27.4	136°20'	4	C_{2h}^5				69,80
Sebacic, $C_{10}H_{18}O_4$										
α	10.10	5.00	15.10	133°48'	2	C_{2h}^5	3°		133	77

and the entire molecule is virtually planar. The two carboxyl groups of one molecule are parallel to each other. The α-form of the odd acids possess a twofold symmetry axis through the central carbon atom, the skeltal chain is slightly twisted and the carboxyl groups of one molecule are rotated in opposite directions. In both series, the packing of the COOH layers seems to dominate the structure of these acids. The symmetry of the even acids allows freedom to the carbon chain in choosing the most convenient position with respect to the carboxyl groups. The skeletal chain and the COOH groups form an approximate plane; the higher the homologue, the more nearly planar is the molecule. However, this planar configuration cannot be achieved for the odd acids, and the chain must be "twisted" in order to fit into the preferred packing of the COOH layers.[73]

In the solid state the even and odd acids have been found to possess a strong alternation of physical properties, such as (1) freezing points, (2) heats of crystallization, and (3) melting points.[83] The lower melting point of the odd acids indicates a relatively high energy content. MacGillavry et al.[73] ascribed this relatively high energy content of the odd members of the series to the fact that the stable configuration of the "free" acid is the planar one, but the preferred packing of the COOH-groups in the crystal forces the odd molecules to "twist". Each odd molecule possesses two twisted bonds in the crystalline state and should have an extra energy of $\sim$ 2 kcal/mole compared with energy of the molecule in the "free" plane configuration.

All members of the α- form even acids have been shown to possess C_{2h}^5 space group symmetry and 2 molecules per unit cell. Succinic acid

is the only member of the even series for which two forms have been reported. In this series the neighboring methylene chains do not have parallel skeletal planes and none of the skeletal planes are parallel to the a- or b-crystal axes.

The α-form odd acids have been shown to possess the space group C_{2h}^6 and 4 molecules per unit cell. The skeletal planes of the neighboring methylene chains are parallel to one another and to the b-axis. However, the β-form crystals of this series have not been studied extensively, and there appear to be discrepancies in the literature. Dupré la Tour assigned a space group C_{2h}^6 to the β-form of pimelic and glutaric acids. However, Van der Helm, using a β-form crystal of azelaic acid grown in this laboratory, found the space group to be C_{2h}^5. Whether or not the skeletal planes are parallel to each other or to a crystal axis was not determined. However, spectral evidence indicates that in the β-form the methylene skeletal planes are parallel to one another and to the b-axis. The difference between the α- and β-forms is apparently in the packing of the COOH-groups. Van der Helm thinks that the gross difference between these forms is that in the β-form the neighboring parallel molecules have their acid groups in the same direction, whereas in the α-form the neighboring parallel molecules have their acid groups in opposite directions.

Vibrational Analyses

The normal coordinate analysis of molecules possessing long methylene chains has posed a formidable theoretical problem. An excellent review of the attempts to solve this problem has been made by Holland.[60] Until recently most vibrational analyses of long methylene chains have

not included the effects of the molecular environment, that is, the intermolecular forces between adjacent extended methylene chains have been neglected. Usually the end groups have also been neglected, and only the motions of the methylene groups have been considered.

If one considers a methylene chain of indefinite length, and assumes solutions consisting of traveling waves in the chain, then the solutions obtained involve sinusoidal functions of the phase difference between the vibrations of adjacent methylene groups on the chain. Each solution defines a set of frequencies for a given type of chain motion which is essentially independent of the chain length. The particular solutions for a chain with N methylene groups obtained by applying boundary conditions consist of a sequence of frequencies corresponding to standing waves. The phase difference between adjacent vibrating units is allowed the values $k\pi/(N + 1)$, where $k = 1, 2, \ldots, N$. Hence each methylene sequence should consist of N vibrational frequencies.

The motions associated with a methylene chain will consist of certain vibrations whose coordinates are either symmetric or antisymmetric with respect to a reflection in the skeletal plane. The spectral activities of these vibrations will depend upon the crystal symmetry. The space group can be used to determine the symmetries and activities of these motions. The normal vibrations in which all unit cells vibrate in phase, the so-called unit cell modes, are most likely to be of sufficient intensity to be observed. These fundamentals are equal in number to the degrees of freedom of a unit cell, and they may be classified according to their behavior under the operations of the symmetry group of the unit cell.

However, to a first order approximation a symmetry analysis based on the site symmetry, the symmetry of an isolated molecule, may yield an adequate interpretation of the grosser details in the vibrational spectra. This approach has been used by several authors[84,85] in studying methylene chain molecules. If the unit cell group of the crystal is used for the analysis, then physically one essentially takes into consideration the coupling of vibrations of occupants of different sites in the unit cell. Thus a band predicted by the site symmetry analysis may be split into components under the unit cell symmetry analysis.[86] Such multiplets have been observed in the methylene vibration bands in crystals which contain more than one molecule per unit cell.[61,62,65]

Recently the extensive experimental work of Holland and Nielsen[61,62,63] on n-paraffins and the related n-fatty acids, and the theoretical computer normal analyses of Snyder and Schachtschneider[66] on the n-paraffins have yielded a great wealth of information on the chain vibrations. The range of frequencies covered by a given methylene vibration sequence has been fairly well established. However, Snyder has indicated that it is not always possible to separate two band sequences when their frequency ranges overlap. In particular, Snyder has shown that the bands in the 1065 - 720 cm^{-1} region of the n-paraffin spectrum commonly referred to as methylene rocking modes actually arise from mixtures of rocking and twisting vibrations. Similarly the 1310 - 1175 cm^{-1} region possesses bands which are due to a mixture of rocking and twisting, although these bands are usually referred to as twisting modes. Throughout this work bands which are predominately rocking modes shall be

designated simply as rocking bands with the understanding that the proper nomenclature should be rocking-twisting. Similarly, predominately twisting modes shall simply be designated as twisting bands.

It has been established by both Holland and Snyder that a given methylene motion should cause a sequence of bands whose frequencies progressively increase or decrease with the phase difference between adjacent methylene groups. Furthermore, the multiplicity or splitting of such bands predicted by the unit cell symmetry analysis has been confirmed by both these authors. Holland has been able to qualitatively explain both the splitting and polarization of the rocking modes by considering the interaction, as modified by crystal form, between an oscillator in one chain and its nearest and next-nearest neighboring oscillators in the adjacent chain. Snyder[66] has been able to calculate the intensities of infrared absorption bands for extended n-paraffin molecules by assigning a dipole moment to the methylene group as a whole.

Drawing heavily on the work of Holland and Nielsen and Snyder and Schachtschneider the chain vibrations are summarized in Table IV-2. The CH_2 - motions have been demonstrated in some cases to be doublets when the unit cell contains more than one molecule. The C-C stretching vibration at 890 cm^{-1} also has been found to be split for such crystals. The information presented in Table IV-2 will be used in interpreting the bands observed in the spectra of the normal dicarboxylic acids.

TABLE IV-2

CHAIN VIBRATIONS

Description	Frequency Range cm^{-1}
CH_2 symmetric stretching CH_2 asymmetric stretching	3000-2800
CH_2 deformation	~ 1475
CH_2 wagging	1400-1175
CH_2 twisting	1300-1175
CH_2 rocking	1050-700
C-C stretching	1150-950
C-C-C angle bending	< 500
skeletal torsional vibrations	< 500

No normal coordinate analysis has been accomplished yet on any normal dicarboxylic acid. Susi[85] did a group theoretical analysis on adipic acid based on the C_i symmetry of the isolated molecule, $HOOC(CH_2)_4COOH$. Since the molecule of adipic acid is approximately planar, Susi classified the infrared vibrations as a_u (in-plane) and b_u (out of plane) motions corresponding to a C_{2h}-symmetry. For such a molecule in the crystal there should be 3n-4 observable fundamentals when n is the number of atoms in the molecule. For adipic acid Susi predicted 56 fundamentals, 29 of species a_g and 27 of species a_u. The presence of two molecules with C_i site symmetry in the C_{2h}^5 unit cell causes each single chain mode to split into components, i.e.,

a_u becomes a_u and b_u, a_g becomes a_g and b_g. The a_u vibrations are polarized in the direction of the monoclinic b-axis, the b_u vibrations are polarized at right angle to the b-axis.

Recently Ananthanarayanan[17] did a group theoretical analysis of adipic acid and sebacic acid, $HOOC(CH_2)_8COOH$, based on the C_{2h}^5 space group symmetry. He predicted 27 Raman active modes each of symmetry a_g and b_g for adipic acid and 45 Raman active modes each for sebacic acid. This is consistent with Susi's work, since Ananthanarayanan took 3n-6 to be the total number of internal vibrations. Actually, he gained little information concerning Raman bands from the unit cell analysis over the site analysis. The unit cell analysis is necessary, however, to account for the dichroism of infrared bands.

Vibrational Spectra

Both Raman and infrared spectra of n-paraffins and the related n-fatty acids have been reviewed adequately by Holland.[60] Furthermore, he has added appreciably to the knowledge on the dichroism of the infrared bands of the longer-chain n-paraffins and n-fatty acids. The papers of Holland and Nielsen have been referred to extensively during the period of this investigation.

While infrared data on long-chain methylene compounds has become more extensive in recent years, Raman data on such compounds are generally lacking. The Raman spectra of the longer-chain crystalline n-paraffins and related compounds have shown fewer bands than predicted by theory.[25] For chains of moderate to short lengths, usually studied as liquids, the number of observed Raman bands more nearly corresponds to the theoretical predictions.[87] Each observed band appears

to be a member of a "band sequence" which can be traced through the spectra of homologues of the n-paraffins. For some sequences the intensities of the bands appear to be independent of the chain length, and for others the bands decrease in intensity with increasing chain length. The bands whose intensities are relatively independent of chain length are predominant in Raman spectra of the longer methylene chain molecules. Bands attributed to end-group vibrations decrease in intensity with chain length. In a preliminary study of the Raman spectra of the alcohol, the monocarboxylic acid, and the dicarboxylic acid with twelve methylene groups forming the skeletal chain have been found to be remarkably similar, the observed frequencies being predominantly chain vibrations. Work on these compounds is presently in progress.

As would be expected, the Raman spectra associated with the dibasic acids consist of bands which may be loosely divided into two groups, bands associated with the carboxyl end-groups and bands associated with the methylene-chain. These bands corresponding to carboxyl end-group vibrations are fixed in number and approximately fixed in frequency, being essentially independent of the chain length. Their intensities, of course, decrease with increasing chain length. The band sequences attributed to methylene chain motions should increase in number with chain units, but this has not been observed.

The first studies on the Raman effect in the crystalline state of dibasic acids were made by B. Anand[88] in 1936. He studied oxalic, malonic, and succinic acids with 4358 A excitation. Only the strongest Raman bands in the spectra of these acids were found, five bands being

reported for succinic acid. During the same period Edsall,[89,90] in a thorough investigation of the ionization of the carboxyl group, reported Raman data on oxalic, malonic, and succinic acid in solutions. While Edsall reported more Raman bands than Anand, many more Raman bands would be expected for the acid in solution. Marignan and Bardet[91] have reported an excellent Raman study on a single crystal of oxalic acid, $HOOC.COOH.2H_2O$. They reported 23 bands between 51 and 1749 cm^{-1} and were able, with the aid of polarization measurements, to resolve many expected splittings of bands.

Recently Ananthanarayan[16,17] has reported Raman data on single crystals of malonic, succinic, adipic, and sebacic acids using Hg-2537 A for the exciting wavelength. The samples of malonic and succinic acids became opaque after two hours exposure and had to be changed. Employing a medium quartz spectrograph and 0.025 mm slit width he obtained the data with exposures of the order of six hours. The adipic and sebacic acid samples required 72 hour exposures. These acids have also been studied by the present author with Hg-4358 A excitation. Except for Raman bands below 200 cm^{-1} and some weak bands, Ananthanarayan's data have been confirmed. Further comment will be made on Ananthanarayan's work when the author's data are presented and analyzed.

In the infrared spectra of methylene chain molecules, contrary to the case of the Raman spectra, the number of bands observed in a homologous series is found to increase with the chain length. However, the intensity again decreases with the chain length, and in polyethylene only a few fundamental bands are observed.[25] Some of the band series may be grouped together, their members in the spectrum of a particular

molecule forming regular spaced "band sequences". The number of bands is found to increase, and the separation decrease as the chain length increases, but the range of frequencies covered by a given sequence remains constant. The chain vibrations and their frequency ranges have been summarized in Table IV-2.

While the Raman spectra of methylene chain compounds of moderate length are dominated by the chain frequencies, the various end-groups of the chains can have an appreciable affect in the 2000 to 500 cm^{-1} region of the infrared spectra. Using a perturbation technique Theimer[92] has calculated that the end-groups should have no appreciable affect on the skeletal vibrations when the number of methylene groups is greater than five. He also showed that the skeletal modes should not be observable in the infrared spectra, but mixing between CH_2- and skeletal vibrations could activate the skeletal modes. It is possible that the strong hydrogen bonding of the acid end-groups of carboxylic acids could also cause activation of the skeletal modes due to the boundary effects.

The infrared spectra of oxalic, malonic, succinic, and glutaric acid were studied in the 5000 to 700 cm^{-1} region by Fichter.[93,94] During the same period Schomann[95] obtained the infrared spectra of adipic, pimelic, suberic, and azelaic acids in the 4000 to 400 cm^{-1} region. He also studied the infrared spectrum in this region of glutaric acid in the solid and liquid phases. Few bands were reported due to the low resolution, and the assignments were rudimentary. The CH and OH stretching, C = O stretching, and CH_2 bending vibrational assignments have stood the test of time, but the assignments below $\sim$ 1400 cm^{-1} have been refined considerably. These early investigators simply assigned

vibrations in this region to "chain oscillations".

Mann and Thompson[96] produced a crude polarized infrared spectrum of adipic acid with unknown orientation and did not add appreciably to the knowledge of the vibrational spectrum. Fleet[97] studied 60 carboxylic acids between 700 and 4000 cm^{-1}. Included in this group were oxalic, malonic and succinic acids. Fleet concluded that there were five bands definitely characteristic of the carboxyl group in these acids. These bands were located at 2500 - 2700 cm^{-1}, near 1700 cm^{-1}, near 1420 cm^{-1}, near 1250 cm^{-1} and near 900 cm^{-1}. No detailed interpretation were made of these bands. Kuratani[98] studied the infrared dichroism of adipic acid crystallized as needles in the 3570 to 2850 cm^{-1} region. He found strong absorption when the electric vector was parallel to the long axis of the needles indicating that the hydrogen bonds are parallel to this axis.

Davison and Corish[99] obtained the infrared spectra of the n-dicarboxylic acids, $HOOC(CH_2)_nCOOH$, with n = 2-8, 10, 14, and 16, in the region from 3500 to 670 cm^{-1} both in the crystalline and the liquid phases. The spectra are shown but the actual absorption frequencies are not tabulated. They reported that the crystalline and liquid spectra of these acids differ appreciably due to the loss of the planar configuration in the liquid phase. No new assignments were made.

Hadži and Sheppard[100] made a study of the infrared absorption bands in the region 1500 to 500 cm^{-1} for several straight-chain mono- and dicarboxylic acids with both COOH and COOD groups. They obtained the spectra of oxalic, malonic, succinic, glutaric, and adipic acids and their COOD derivatives. They reported that the COOH group is responsible

for strong absorption bands in the regions 1420 ± 20, 1300 ± 15 and 935 ± 15 cm^{-1}. They assigned these absorptions to coupled OH bending and C-O stretching vibrations occurring in the plane of the $(COOH)_2$ dimeric ring and to out-of-plane OH bending vibrations, respectively. The COOD group, they reported, caused bands at 1350 ± 50, 1050 ± 10 and 675 ± 25 cm^{-1}, which they assigned, respectively, to the C-O stretching mode and the in-plane and out-of-plane OD bending vibrations. They are uncertain with regard to assignments of COOH vibrations between 700 and 575 cm^{-1}.

Later Bratož, Hadži, and Sheppard[101] made a study of 27 carboxylic acids with COOH and COOD groups in the region from 3700 to 1500 cm^{-1}. Malonic, succinic, glutaric, and adipic acids and their COOD derivatives were studied in Nujol mulls. They reported three prominent features in the spectra, a broad $\nu_{OH}(\nu_{OD})$ absorption centered at 3000 cm^{-1} (2300 cm^{-1}), its weaker satellite bands centered near 2650 cm^{-1} (2100 cm^{-1}), and the well known C = O stretching vibration centered at 1720 ± 30 cm^{-1}. The significance of this paper lies in the thorough investigation of the satellite bands and their interpretation as sum bands, involving lower frequency COOH fundamentals responsible for the main ν_{OH} absorption regions. Prior to this investigation these satellite bands had been interpreted by some authors[102,104] as difference bands of the type $\nu_{OH}-\nu'$, where ν' is a Raman active hydrogen bond stretching fundamental ($\sim$300 cm^{-1}). However, this explanation requires a corresponding band $\nu_{OH}+\nu'$ near 3300 cm^{-1} of greater intensity than the 2700 cm^{-1} difference band. No such band was observed. Furthermore, temperature studies did not reveal a great reduction in

intensity due to the Boltzmann factor which would be expected for a band of the form $\nu_{OH}-\nu'$. It is evident that, while hydrogen bonding may add to the broadening of the ν_{OH} bands and the appearance of the satellite bands, it can not be the major cause.

Susi[85] recently undertook an extensive study of the infrared spectra of crystalline adipic acid and its deuterated analogues in the hope that his results could be carried over to related compounds of higher molecular weight. He studied $HOOC(CH_2)_4COOH$, $DOOC(CH_2)_4COOD$, $HOOC(CD_2)_4COOH$, and $DOOC(CD_2)_4COOD$ in the 4000 to 400 cm^{-1} region and made dichroism measurements in the 4000 to 650 cm^{-1} region. Of the 27 possible infrared a_u active fundamentals, 19 were assigned. Extensive use has been made by the author of Susi's work, and it will be referred to in the interpretation of the spectra obtained.

Based primarily on the investigation of Holland and Nielsen on stearic, $CH_3(CH_2)_{16}COOH$, palmitic, $CH_3(CH_2)_{14}COOH$, acids and the study of adipic acid, $HOOC(CH_2)_4COOH$, by Susi, a summary of bands associated with the COOH group is given in Table IV-3. This table will be used in assigning COOH fundamentals vibrations in the spectra of the dicarboxylic acids. Evidence will be given to show that two bands occurring in the 500 to 550 cm^{-1} region of such spectra are also due to COOH group vibrations.

TABLE IV-3

COOH CHARACTERISTIC FREQUENCIES

Approximate Frequency cm^{-1}	Description
3000	O-H stretching
1690	C=O stretching
1430	C-O stretching, O-H bending
1280	O-H bending, C-O stretching
930	O-H bending
690	O=C-OH bending

Hydrogen Bonding

Many organic molecules, in the liquid and solid phases and occassionally in the vapor phase, are bonded together in dimers and higher polymers by the low energy hydrogen bond. The hydrogen bond energy is only of the order of 6 kcal/mole and the bond is extremely important in biological systems. In recent years the nature of the hydrogen bond has been undergoing thorough theoretical and experimental investigations.[102-107] One method of studying the hydrogen bond is by spectroscopy of compounds which are known to form such bonds.

In the dicarboxylic acids, the hydrogen bonding stretches over many molecules, the O....O distance is decreased from 2.8 A to approximately 2.5 A, and the bond energy is doubled to 10 kcal/mole. Calculations by Coulson and Danielsson[106] have shown that the shorter hydrogen bonds such as occur in the carboxylic acids may be less electrostatic in nature than the longer hydrogen bonds.

The hydrogen bond is known to have an influence on molecular vibrations, and this may be observed in both the infrared and the Raman spectra. Based on previous investigations[105,108] we might expect the following effects of hydrogen bonding on the vibrational spectra of the dicarboxylic acids: (1) shifts in the ν_{OH}, δ_{OH}, ν_{C-O} and $\delta_{C=O}$ frequencies, (2) appreciable broadening and enhancement of the ν_{OH} band, and (3) appearance of low frequency bands due to hydrogen bond stretching, $\nu_{(ROH)\cdots(OR')}$. The hydrogen bond stretching vibration is essentially a lattice vibration, but is slightly higher in frequency than the intermolecular vibrations which arise from the action of van der Waals forces.

Ananthanarayanan[17] has recently interpreted certain low frequency Raman bands he observed in adipic and sebacic acids as hydrogen bond virbrations. Making use of a potential proposed by Lippincott, Finch and Schroeder[109] he evaluated theoretically the vibrational frequencies of the bond. He found good agreement between these and the experimental values. However, in the Raman spectrum of sebacic acid he reports that some of the intermediate and higher hydrogen bond transitions were not observed. These missing bands were not explained.

CHAPTER V

RAMAN AND INFRARED DATA ON NORMAL DICARBOXYLIC ACIDS

Introduction

No vibrational study based on both infrared and Raman data of a series of dibasic acids has been noted in the literature. Infrared polarization data have been reported for only adipic acid, $HOOC(CH_2)_4COOH$, and no Raman data have been reported for any of the regular higher homologues of the odd-chain dibasic acid series. A study on a series of dibasic acids, $HOOC(CH_2)_nCOOH$, will be reported here. Raman data have been obtained for acids with n = 1 to 8, and 12, and for $DOOC(CH_2)_5COOD$. Furthermore, polarized infrared data have been obtained for single crystals of the acids with n = 3 to 8, and 12, and for $DOOC(CH_2)_7COOD$.

Raman Spectra

The Raman spectra were obtained with the technique described in Part I. The samples were purchased from Eastman Organic Chemicals, Distillation Products Industries, Rochester, N. Y., Mann Research Laboratories, Inc., New York, N. Y., Harchem Division of Wallace and Tiermann, Inc., Belleville, N. J., or Calbiochem, Los Angeles, California. All of these samples were of C. P. or higher grade, unless noted. Six of the samples were fluorescent as received and required treatment for removal of the fluorescent impurities.

Each sample was tested for fluorescence by careful investigation when irradiated with a short wave (Hg-2537A) ultraviolet lamp and a long wave (Hg-3660A) u.v. lamp. Some samples were found to be fluorescent under both s.w. and l.w. radiation, while others were fluorescent under either one or the other. Long wave fluorescence was more of a problem than s.w. fluorescence in obtaining the Raman spectrum; for a sample which is fluorescent under the l.w. lamp is more likely to be fluorescent under the 4046 A and 4358 A wavelengths. Moreover, it is highly improbable that the shorter wavelength Hg-lines penetrate the Pyrex glass of the focal-point lamp or the thick condenser lenses and the interference filter.

If a sample was found to be fluorescent, one or more of several techniques were used in an attempt to decrease the fluorescence: (1) Recrystallization of the sample from an appropriate solvent. (2) Boiling the sample in an appropriate solvent with 2% by weight of activated charcoal, filtering while hot, and allowing recrystallization to occur by cooling. (3) Distillation of the sample under a vacuum. Some degree of success was had with most samples with techniques (1) and (2). Both of these techniques appeared to work best with a particular solvent for any given sample. Undoubtedly, technique (1) works well if the impurity causing the fluorescence remains in the solvent when recrystallization takes place. Whenever technique (1) or (2) was used, the sample was vacuum-dried to insure removal of the solvent.

It was noted that some samples which were initially weakly or nonfluorescent could become highly fluorescent over a period of time after exposure to air. This was noted particularly with the n-paraffins and n-fatty acids.

Twenty-eight exposures were made of the nine dibasic acid samples, the longest exposure times being 72 hours. An iron arc spectrum was also recorded on the film to help determine the Raman shifts. The quality of the Raman spectra obtained varied. This was due in part to residual sample fluorescence. Unfortunately, the primary interference filter began to fail during the study, and an inferior filter had to be used. This also caused the quality of some Raman spectra to be less than desired. Moreover, it was found that sample thicknesses of less than 0.5 mm do not yield good Raman spectra. However, the fineness of some crystalline powders required this small thickness.

Malonic acid, $HOOC(CH_2)COOH$, obtained from Mann was found to be slightly shortwave fluorescent. It was treated by technique (2) with water as the solvent with no appreciable success. A 72 hour exposure with 75μ slit width of a 2.6 mm thick sample was made of which a densitometer tracing is given in Appendix II. This spectrum will not be interpreted here, since the structure of the molecule and the unit cell differ substantially from those of the other dibasic acids.

Succinic acid, $HOOC(CH_2)_2COOH$, also obtained from Mann was found to be slightly s.w. fluorescent and heavily l.w. fluorescent. Technique (2) was used with water as the solvent, and the fluorescence was greatly diminished. A 72 hours exposure with 75μ slit width was made of a 1.5 mm thick polycrystalline sample. A densitometer tracing of this film is shown in Fig. V-1, and the Raman shifts are tabulated in Table V-1. It is not known whether this was α- or β-form succinic acid. Ananthanarayanan[16] has obtained Raman spectra of both malonic and succinic acids using Hg-2537 A excitation. This spectrum confirms his data, except for

bands below 200 cm^{-1} and some very weak bands, many of which appear to be shoulders on other Raman bands or on the approximately twenty Hg-lines superimposed on Ananthanarayanan's spectrum. Some of the very weak Raman bands reported by him may not be real.

Samples of glutaric acid, $HOOC(CH_2)_3COOH$, were obtained from both Eastmann and Mann. The samples were slightly tan colored and were found to be highly fluorescent. They were treated twice with technique (2) with water as the solvent. This did not noticeably diminish the fluorescence. One of the samples was then subjected three times to technique (2) with benezene as the solvent. While the fluorescence was still evident, it was diminished. Four 72 hour exposures of a 0.6 mm sample (slightly colored) were made. Whether this was the α- or β-form is not known. While the spectra allowed the measurement of a number of Raman bands, no densitometer tracing was made because of the residual fluorescence background. The observed Raman bands are listed in Table V-2.

Adipic acid, $HOOC(CH_2)_4COOH$, obtained from Mann was found to be non-fluorescent. A 72 hour exposure was made of a 1.3 mm thick sample. The densitometer tracing of this film is shown in Fig. V-2. The Raman bands are listed in Table V-3. This Raman spectrum compares favorably with the one obtained by Ananthanarayanan.[17]

The sample of pimelic acid, $HOOC(CH_2)_5COOH$, also obtained from Mann, showed slight l.w. fluorescence. Technique (2) was used with water as a solvent and this produced satisfactory improvement. A 1.0 mm thick sample of uncertain crystal form was exposed for 72 hours. The densitometer tracing is shown in Fig. V-3, and the Raman bands are listed in Table V-4.

A sample of partially deuterated pimelic acid, $DOOC(CH_2)_5COOD$, was prepared by dissolving the acid in heavy water and allowing recrystallization by cooling to occur. This was repeated three times to insure the deuteration of nearly all carboxyl groups. However, it was found that the sample so prepared was fluorescent. This procedure was repeated several times, always with the same result. Three 72 hour exposures were made of such samples, approximately 1 mm thick. The background was considerable, and a densitometer tracing was therefore not made. The bands observed are tabulated in Table V-4. The deuteration of the carboxyl groups appears to have been rather complete, since an OH related band at 899 cm^{-1} shifted to 870 cm^{-1}, and the O=C-O bending vibration at 673 cm^{-1} shifted to 638 cm^{-1}.

A non-fluorescent sample of suberic acid, $HOOC(CH_2)_6COOH$, was obtained from Mann. While attempting to grow crystals from ethyl ether in a sealed tube heated to 100°C then allowed to cool, several explosions occurred and rendered this sample useless. A second sample obtained from Mann proved to be fluorescent and did not respond well to treatment. Slight improvement was shown by recrystallization from a hot saturated solution in benzene. Also, during the study of suberic acid the primary interference filter decreased in peak transmission, causing a decrease in the observed Raman band intensities. Three exposures of 72 hours length of a 0.3 mm sample were made. None of these Raman spectra are considered satisfactory. The bands observed are reported in Table V-5.

Two samples of azelaic acid, $HOOC(CH_2)_7COOH$, were obtained from Calbiochem and one from Eastmann. The samples from Calbiochem were pale yellow in color, highly fluorescent, and did not respond to treatment by

any of the three techniques. The sample from Eastmann was pale tan in color and also fluorescent. However, three treatments of this sample by technique (2) with water as a solvent caused a decrease in the fluorescence but did not change the color. Three 72 hour exposures with an inferior primary filter were made with a 0.5 mm thick sample of uncertain crystal form. The background in all the exposures is considerable, and the spectra are not considered to be very complete. The Raman bands observed are reported in Table V-6. During the infrared investigation of this acid large crystals of the β-form were grown (4 mm x 2 mm x 50 μ) and an attempt was made to use these as a Raman sample, but the fluorescence was found to be prohibitively high.

Sebacic acid, $HOOC(CH_2)_8COOH$, was obtained from Harchem. The sample was somewhat fluorescent, but three recrystallizations from concentrated nitric acid decreased the fluorescence considerably. A 72 hour exposure was made of a 0.6 mm thick sample during the period when the interference filter was failing. The densitometer tracing is shown in Fig. V-4. The Raman bands are listed in Table V-7. This spectrum does not show quite as many Raman bands as that recently obtained by Ananthanarayanan.

A tetradecanedioic acid, $HOOC(CH_2)_{12}COOH$, sample of practical grade was obtained from Eastmann. It proved to be fluorescent, but responded well to two recrystallizations from concentrated nitric acid. However, the sample thickness required was 0.3 mm and the spectra obtained so far on three attempts are far from complete. The Raman bands measured on a 72 hour exposure are listed in Table V-8. Work is continuing on this sample in the hope that the Raman spectrum can be

improved, since the sample is non-fluorescent.

Since the Raman spectra of these acids were obtained on powdered samples, the crystal form of the odd-acid samples is somewhat uncertain. The even-acid samples were undoubtedly of the α-form, since no other form has been found. While the polarized infrared spectra of different polymorphs of a methylene-chain compound have been demonstrated to be quite different, no such difference has yet been demonstrated for the Raman spectra.

Infrared Spectra of Single Crystals

Any fundamental mode of vibration which is accompanied by a changing electric dipole moment is capable of absorbing radiation. This changing electric dipole moment is a vector quantity having a well-defined direction in a crystal. The crystal will be incapable of absorbing radiation that is polarized in a plane perpendicular to this direction. Hence, the absorption of radiation by a particular mode will vary with the angle that the electric vector of the plane polarized radiation makes with the electric dipole direction characteristic of the vibration.

Spectral studies with polarized radiation give information about the direction of such oscillating dipoles with respect to the crystal axes. Such data can then be interpreted in terms of molecular and crystalline structures. However, a problem exists in relating the structually significant directions defined in the absorbing crystal and the directions of propagation and polarization of the radiation defined outside the crystal. This problem has been considered by Newman and Halford.[110] Ideally, a crystal orientation should be choosen such that plane polarized radiation may transverse it without suffering refraction

or a change of polarization. Plane polarized radiation incident upon an arbitrarily oriented, anisotropic, absorbing crystal will suffer refraction and changes in polarization. For certain crystals the dielectric and conductivity tensors possess parallel principal axes. If the radiation is incident normal to a crystal face, whose surface is parallel with a plane containing two of these principal axes, and if the electric vector is polarized parallel to one of these principal axes, then the radiation should undergo no changes other than possible absorption in transversing the crystal.[111]

The directions of the eigenvectors of the dielectric and conductivity tensors can depend upon the frequency of the light. For certain crystal systems, fortunately, these axes are fixed by the symmetry and are independent of the frequency. For monoclinic crystals, such as dicarboxylic acids, one axis of the complex dielectric tensor (polarization axis) is fixed by symmetry along the b-axis and the other axes are unrestricted. In obtaining polarized infrared data on a monoclinic crystal it is advantageous to have the light incident normal to a crystal face containing the crystallographic b-axis with the polarized electric vector incident parallel or perpendicular to this symmetry-fixed axis. The radiation should transverse the crystal with minimal changes in character.

For certain molecular crystals the molecules will possess either a plane of symmetry or near plane of symmetry, and the normal modes may be divided into two classes: symmetric and antisymmetric with respect to a reflection in this plane. Consequently the dipole moment generated by a given vibration will be parallel or perpendicular to the symmetry

plane of the molecule. With knowledge of the placement of such planar molecules in the unit cell, the polarization characteristic of in- and out-of-plane vibration can be easily ascertained. These transition moments will frequently be parallel to crystallographic axes. If possible, the crystal should be choosen such that it possesses a face parallel to these two axes. Maximum information will then be gained by obtaining the spectrum with the light incident normal to this crystal face with the incident polarized electric vector parallel first to one transition moment and then the other.

If the molecules in the crystal are not planar, the situation becomes much more complicated. If may not be possible to obtain polarized data which will yield any very useful information. Severe difficulties will also be encountered with monoclinic crystal containing planar molecules if the crystal possesses a heavy mosaic or other imperfections.

There are technical difficulties in growing suitable crystals to allow such data to be obtained. The development of the reflecting microscope for use with the Perkin-Elmer spectrometer has reduced the area requirement of a crystal to one millimeter square or slightly less. Ideally, the sample should be a perfect single crystal of appropriate thickness with smooth surfaces large enough to admit all the beam utilized by the reflecting microscope.

The use of a reflecting microscope also introduces problems. No longer is a plane parallel light beam incident upon the crystal. The incident polarized light is in the form of a convergent beam. Thus, the spectrum obtained is a superposition of the desired spectrum plus the spectrum characteristic for the electric vector vibrating perpendicular

to the crystal face. This problem is mainly serious when a band possesses a strong component in one direction and a weak component in another direction. When observing with the electric vector parallel to the weak component direction, it is difficult to determine with certainty that the observed band is real and not in fact due to slight absorption by the strong band caused by the polarized convergent beam.

For crystals of the even dibasic acids, the molecules are nearly planar and the unit cell fundamental vibrations are polarized with components parallel and perpendicular to the b-crystallographic axis, which is also the symmetry-fixed dielectric tensor axis. A detailed unit cell analysis will be presented in Chapter VI. The even-acid crystals tended to grow as flat platelets with their large face parallel to the crystallographic ab plane. Hence, the maximum information was gained by obtaining the two polarized spectra with the light ray incident normal to the crystal face parallel to the ab-plane with the incident electric vector parallel to the a-and then the b-axis, respectively.

The crystals of the odd acids do not contain molecules which are even nearly planar. Hence, the problem of choosing suitable directions of incidence and polarization to obtain the spectra is much more complicated. It would appear, as will be explained in Chapter VI, that the skeletal planes of the methylene chains of the α- and β-forms of the odd acids are parallel to one another and to the bc-plane. Hence, it is suitable also in these cases to let the incident electric vector be polarized in the a-and b-directions, respectively. However, only for azelaic acid could crystals be grown for which the orientation of the axes was known with certainty.

Crystal Growing Techniques

Up to the present time polarized infrared radiation studies have not been applied extensively. Unfortunately, the growing of suitable crystals is an art which can only be acquired through considerable experience — trial and error. A technique used in growing single crystals of n-paraffins or n-fatty acids is not necessarily useful in growing single crystals of the related n-dicarboxylic acids.

The previously mentioned papers on x-ray diffraction of single crystals of these compounds were somewhat useful in determining the proper solvent. However, the crystal sizes required for x-ray diffraction studies and polarized infrared radiation studies are entirely different. While x-ray diffraction work can use a thick crystal, the large absorption in the infrared, primarily by the carboxyl groups, requires the use of a much thinner crystal. While Holland[60] was able to use crystals with thicknesses up to 100 μ when studying the n-monocarboxylic acids, the effective doubling of the number of end groups in the dicarboxylic acids required the use of crystals of 50 μ thickness or less. Even with the thinnest crystals grown, it was difficult to study the intense carboxylic group bands. No crystals were grown sufficiently thin to allow data to be obtained for the bands caused by CH and OH stretching (2800-3300cm^{-1}).

The n-paraffins and n-fatty acids have a tendency to grow as thin flakes parallel to the ab-plane and can be cleaved easily along this plane. This property allows some degree of choice in sample thickness. The easy cleavage probably occurs on planes composed of methyl groups bound together by van der Waals' forces. However, the dibasic acids are bonded by strong hydrogen bridges which tend to cause crystal growth

along the c-axis. The crystals were found to grow as needles along the c-axis in some cases, and in thick planar habits in other cases. The hydrogen bridge makes cleavage along an ab-plane almost impossible to achieve. Hence, sample thickness must be governed by the technique used to grow the crystal. Contrary to the slow evaporation or cooling of a solution used to produce good crystals of n-paraffins and n-fatty acids, a hastening of these two processes was necessary in most cases to produce sufficiently thin crystals of dibasic acids. Each acid presented an individual problem, no two acids actually responding to the same technique. No general procedure can be given for obtaining good crystals, but the technique utilized to grow each crystal for which infrared data were obtained will be mentioned briefly.

Experimental Results

To date no crystal of succinic acid $HOOC(CH_2)_2COOH$, has been grown which would allow useful polarized infrared data to be obtained. Succinic acid was found to favor a needle-like crystal growth in all solvents tried. The needles are essentially single crystals as shown by examination with a polarizing microscope. An effort was made to lay a number of needles side by side so as to construct a sample of suitable area, but the spectrum obtained was not of value.

Glutaric acid, $HOOC(CH_2)_3COOH$, usually grew in a thick irregular pinacoid prism and dome configuration with twinning occurring. However, thin essentially single crystalline plates could be obtained by evaporation of a water solution at $\sim$ 50°C. It proved difficult to ascertain either the crystal habit or form. These crystals showed numerous striations which are thought to be parallel to the ac-plane. The α-form,

the polymorph stable at room temperature, undergoes a transition to the β-form at 74°C. It will be assumed that the crystal whose spectra are shown in Fig. V-5 is of the α-form and that the electric vector in the incident light was approximately parallel and then perpendicular to the a-axis. This assumption is based on a comparison of the polarization of the bands due to the OH rocking motion ($\sim$ 935 cm^{-1}) and the CH_2 rocking motion ($\sim$ 730 cm^{-1}) in the spectrum of glutaric acid and the spectra of other acids whose form and habit are well known. Furthermore, the crystal of adipic acid whose habit and form were determined by x-ray diffraction had striations on the crystal face parallel to the ac-plane similar to those observed on glutaric acid crystals. The infrared and Raman bands are listed in Table V-3.

Adipic acid, $HOOC(CH_2)_4COOH$, was found to crystallize from several solvents in various configurations, few of which were suitable for use as infrared samples. The crystal used to obtain the spectrum shown in Fig. V-6 was grown by evaporation of an ethyl acetate solution at 40°C. An x-ray diffraction study of this crystal by Van der Helm[80] showed it to possess a planar growth along the $\bar{1}1\bar{1}$ crystallographic plane. The methylene chains, therefore, make an angle of approximately 20°C with respect to the plane of the crystal. Hence the incident polarized radiation in the spectra shown in Fig. V-6 had its electric vector approximately parallel to the c-axis with a small component in the direction of the a-axis, and approximately parallel to the b-axis, respectively. Since Susi[85] made an extensive polarized spectral study of adipic acid from 3000 to 600 cm^{-1}, this spectrum is primarily of interest from 600 to 400 cm^{-1}. The infrared and Raman bands are listed in Table V-3.

As in the case of glutaric acid thin, heavily striated, essentially single crystalline plates of pimelic acid, $HOOC(CH_2)_5COOH$, were produced when a water solution was allowed to evaporate at approximately 50°C. Such a crystal was used to obtain the spectrum shown in Fig. V-7. It is believed to be of the α-form, since a transition to a different form was found to occur when it was heated to 80°C. The spectrum of this higher-temperature form is shown in Fig. V-8, and since it closely matches the spectrum of the β-form of azelaic acid, it is assumed that it represents the β-form of pimelic acid. It has been established that in the α-form of glutaric and pimelic acids the skeletal planes are coplanar with one another and with bc-plane. Hence, the CH_2 rocking motion, an out-of-plane motion, is polarized in the a-direction. The spectrum of β-azelaic acid indicates that the CH_2 rocking bands are so polarized. Hence the chains in the β-form of these acids are probably also coplanar to the bc plane. Based on the dichroism of the CH_2 rocking band of lowest frequency in the spectra of the β-form of pimelic acid, the assumptions concerning the polarizations indicated in Fig. V-8 were made. Since the β-form was derived by a transition from the α-form, the assumed polarization directions were carried over to the spectrum of the α-form shown in Fig. V-7.

Suberic acid, $HOOC(CH_2)_6COOH$ was found to grow very small, thin planar crystals when a water solution was allowed to evaporate at room temperature. When examined with a polarizing microscope the crystals had the shape characteristic of the α-form with the large face parallel to the crystallographic ab-plane as shown in Fig. IV-1. On all crystals grown there were usually one or two thin ridges of growth on the b-axis,

that is, small plates parallel to the bc-plane and inclined to the ab-plane. The β angle, the angle between the a-and c-axes, was easily observed, making the a, b, and c axes easy to determine. The infrared spectra obtained with the radiation incident normal to the ab-plane and with the electric vector parallel to the a-axis and to the b-axis, respectively, are shown in Fig. V-9. The vibrational bands of suberic acid are given in Table V-5.

Azelaic acid, $HOOC(CH_2)_7COOH$, was found to crystallize in rectangular plates when a hot saturated water solution was allowed to cool or when a water solution was allowed to evaporate rapidly. The shapes of the rectangular plates are characteristic of the β-polymorph shown in Fig. IV-1. The β angle was measured with a microscope and found to be 136° 30′, which confirmed the β-form. Later x-ray diffraction studies showed this angle to be 136° 20′ and the space group to be C_{2h}^5.[80] The infrared spectra with the radiation incident normal to the ab-plane and the electric vector parallel to the a-and b-axes, respectively, are shown in Fig. V-10.

An effort was made to cleave thin platelets parallel to the bc or ac planes from the planar β-azelaic crystals. However, the brittleness of these crystals made such an undertaking fruitless.

An attempt has been made to grow α-azelaic acid crystals from a warm saturated solution of acetone, but the results are not conclusive at present. While the crystals obtained possess angles which might indicate that they are of the α-form, and the infrared spectrum differs from that of the β-form, heating this crystal to 100°C has not produced the expected α- to β-form transition.

Since azelaic acid crystallizes from a water solution, a partially deuterated sample, $DOOC(CH_2)_7COOD$, was prepared by cooling a saturated solution of azelaic acid in heavy water. The sample was allowed to crystallize several times in this manner to insure effective deuteration. The crystals thus grown were similar in shape to the previous crystals but they were smaller and thinner. The polarized infrared spectrum of such a crystal is shown in Fig. V-11. The infrared and Raman bands of $HOOC(CH_2)_7COOH$, and the infrared bands of $DOOC(CH_2)_7COOD$ are listed in Table V-6.

Sebacic acid, $HOOC(CH_2)_6COOH$, was found to grow small crystals by evaporation of either an ethyl acetate or ethyl alcohol solution at approximately 40°C. The polarized spectrum of a crystal grown from a ethyl acetate solution is shown in Fig. V-12. The crystal had the shape characteristic of the α-form; and it was easy to locate the crystallographic axes with the use of a microscope. The vibrational bands of sebacic acid are listed in Table V-7.

Small single crystals of tetradecanedioic acid, $HOOC(CH_2)_{12}COOH$, were grown by slow evaporation of an isopropyl ether solution at room temperature. The crystal used to obtain the spectrum shown in Fig. V-13 had the α-form shape. Table V-8 gives the vibrational bands determined for this sample.

A study was undertaken to obtain the polarized infrared and Raman data on samples of myristic acid, $CH_3(CH_2)_{12}COOH$, and myristic alcohol, $CH_3(CH_2)_{12}CH_2OH$, to compare with the data on tetradecanedioic acid. The polarized infrared spectra have been obtained for the C-form of myristic acid and the α-form of myristic alcohol. These spectra and tables of

the observed bands are presented in Appendix III. The Raman spectra have been obtained only in a rudimentary fashion, and work is now in progress to improve these spectra.

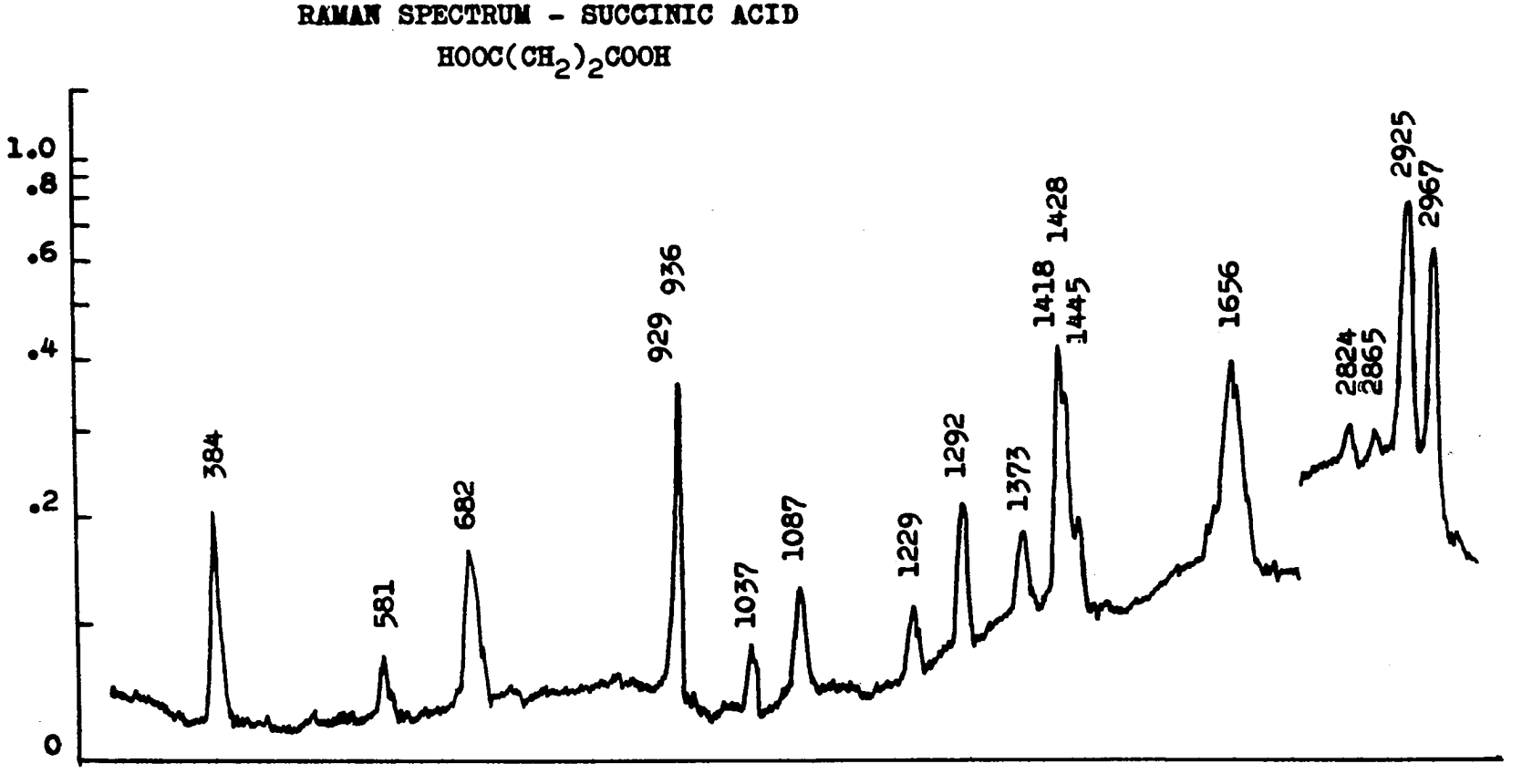

RAMAN SPECTRUM - SUCCINIC ACID
HOOC(CH2)2COOH
1.0
.8
.6
.4
.2
0
384
581
682
929
936
1037
1087
1229
1292
1373
1418
1428
1445
1656
2824
2865
2925
2967

Figure V-1

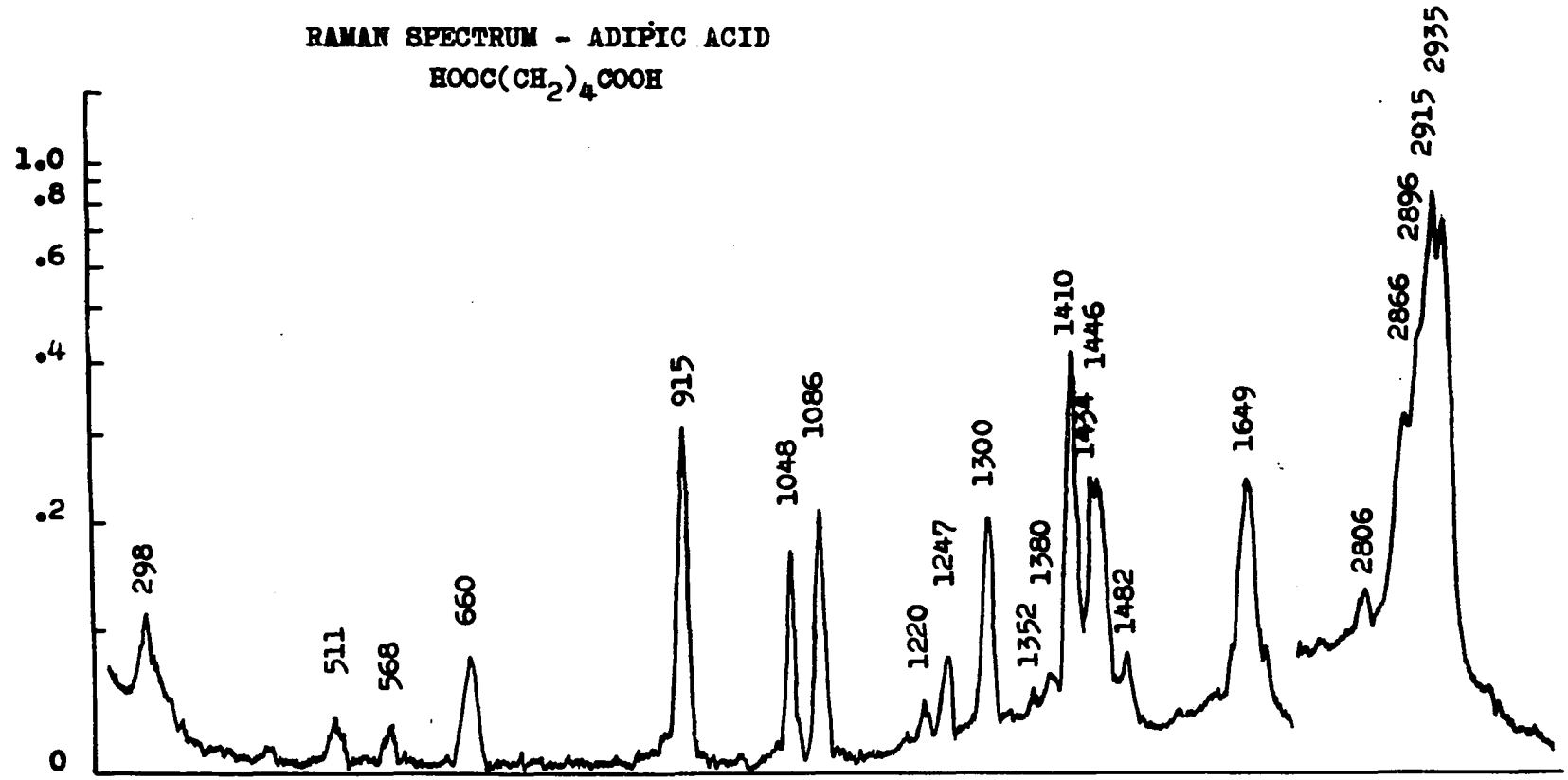

RAMAN SPECTRUM - ADIPIC ACID
HOOC(CH2)4COOH
1.0
.8
.6
.4
.2
0
298
511
568
660
915
1048
1086
1220
1247
1300
1352
1380
1410
1446
1482
1649
2806
2866
2896
2915
2935

Figure V-2

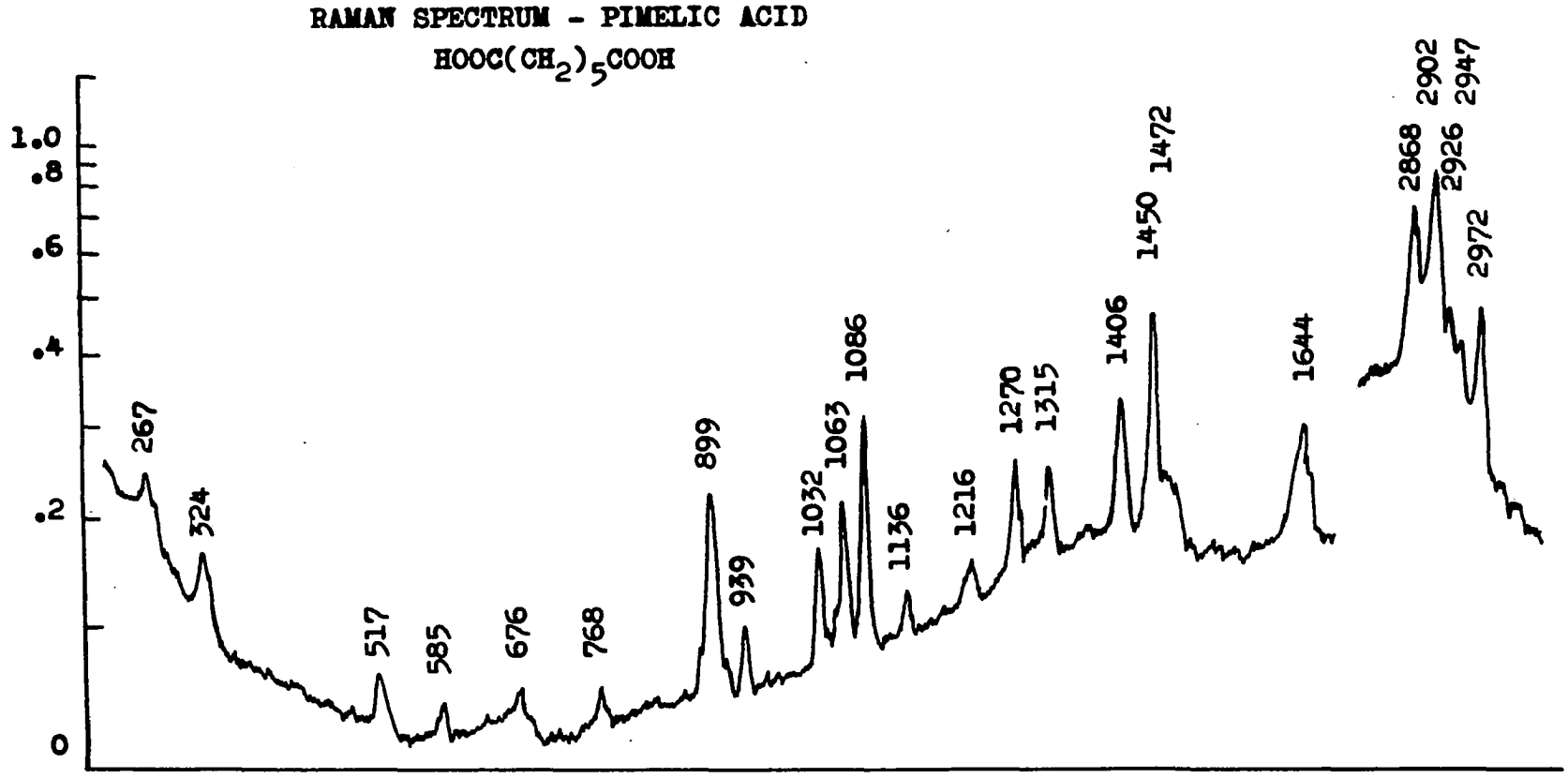

RAMAN SPECTRUM - PIMELIC ACID
HOOC(CH2)5COOH
1.0
.8
.6
.4
.2
0
267
324
517
585
676
768
899
939
1032
1063
1086
1136
1216
1270
1315
1406
1450
1472
1644
2868
2902
2926
2947
2972

Figure V-3

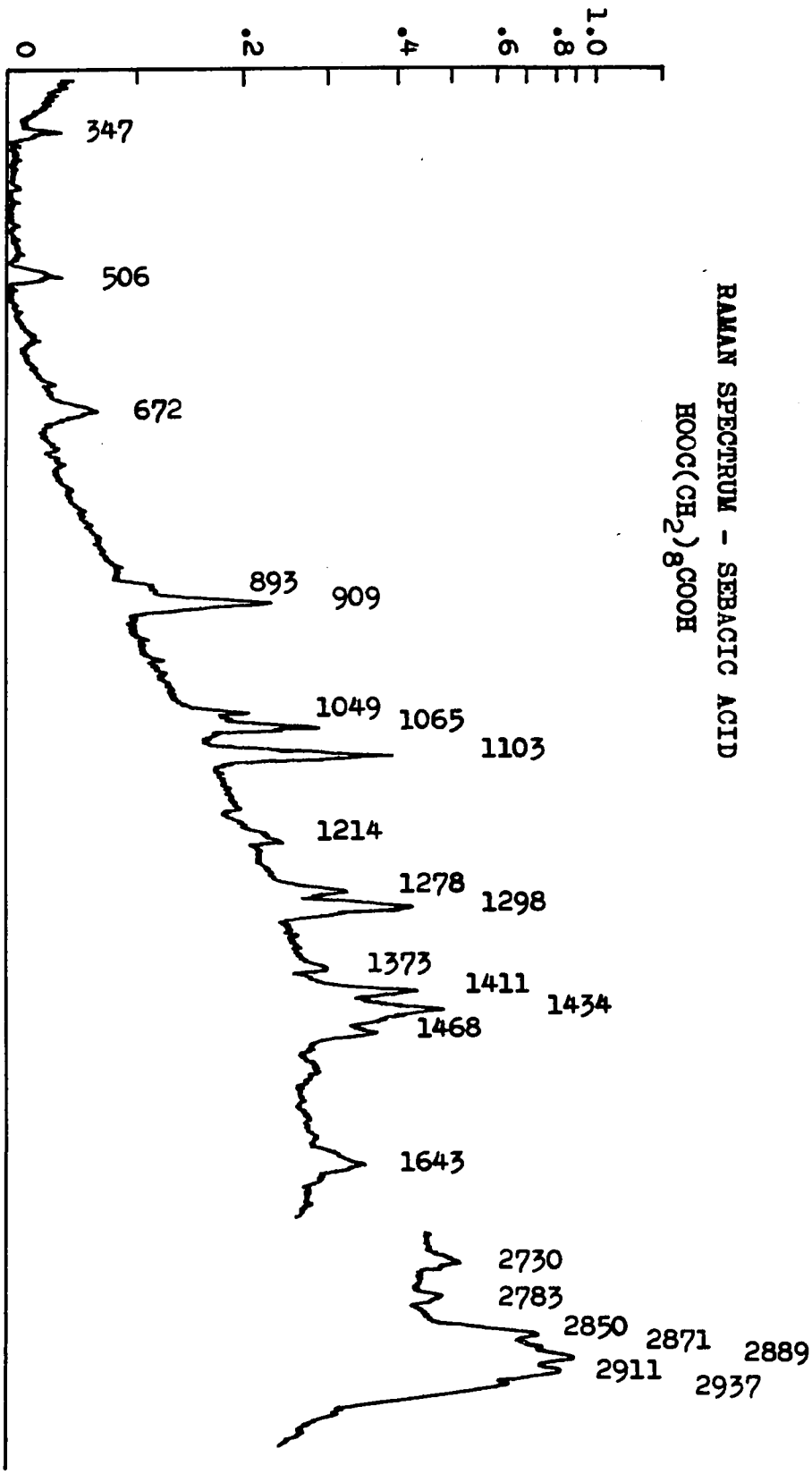

0
.2
.4
.6
.8
1.0
347
506
672
893
909
1049
1065
1103
1214
1278
1298
1373
1411
1434
1468
1643
2730
2783
2850
2871
2889
2911
2937
RAMAN SPECTRUM - SEBACIC ACID
HOOC(CH2)8COOH

Figure V-4

TABLE V-1

RAMAN BANDS OF CRYSTALLINE SUCCINIC ACID
$HOOC(CH_2)_2COOH$

Wave Number	Intensity[a]	Interpretation[b]
2967	vs	asym. CH_2 st
2925	vs	sym. CH_2 st
2865	w	2x1445 = 2890
2824	w	2x1428 = 2856
		2x1418 = 2836
1656	vs	C=O st
1445	w	CH_2 d
1428	s	(ip) O-H b, C-O st
1418	vs	α- CH_2 d
1373	w	CH_2 w
1292	m	CH_2 t
1229	w	sk
1087	m	
1037	w	
936	vs	sk (op) O-H b
929	m	
682	m	(ip) O-C=O b
581	w	COOH
384	s	sk, H···O st[c]

[a]The following abbreviations are used: s strong, m medium, w weak, v very

[b]The meaning of the symbols used are as follows: st stretching, d deformation, b bending, w wagging, t twisting, sk skeletal, (ip) in-plane,(op) out-of-plane.

[c]This band may be due to coupled skeletal and hydrogen bond vibrations.

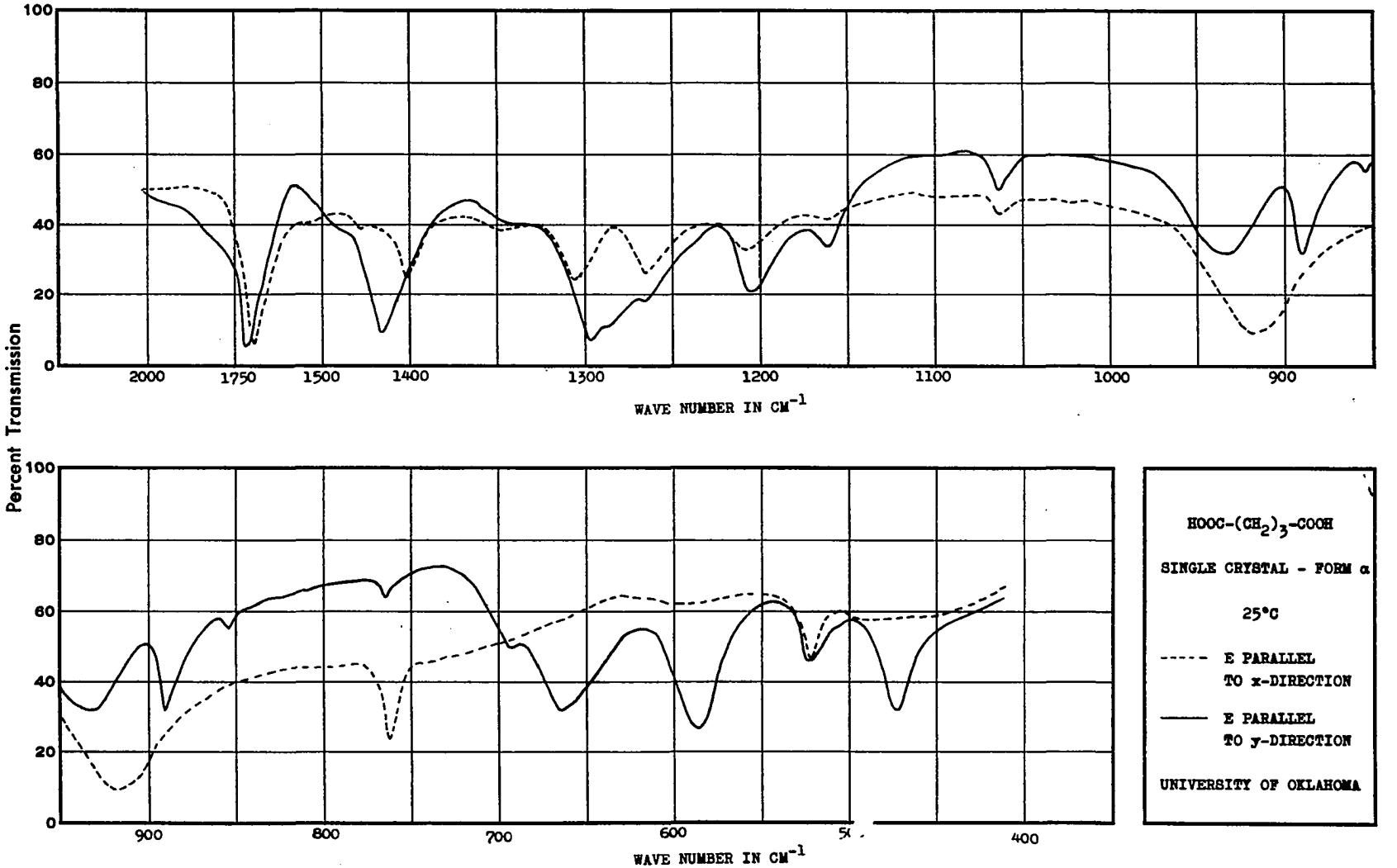


Fig. V-5. Infrared Spectrum of the α-Form of $HOOC(CH_2)_3COOH$; Radiation Incident Normal to the xy-Plane. (See footnote b, Table V-2)

TABLE V-2

VIBRATIONAL BANDS OF CRYSTALLINE GLUTARIC ACID
$HOOC(CH_2)_3COOH$

Infrared			Raman		Interpretation[d]
Wave Number	Intensity[a] and Polarization[b] (Fig. V-5)		Wave Number	Description[c]	
			2977	s	asym. CH_2 st
			2968	s	
			2907	vs	sym. CH_2 st
			2890	vs	
1717*[e]	s	y			C=O st
1695*	s	x			
			1644	s,d	
			1464	w,sh	CH_2 d C-O st, (ip) O-H b
1431	s	y			
			1416	s	α-CH_2 d
1404	mw	x			
			1335	vw	C-O st, (ip) O-H b, CH_2 w, t
1306	w	x			
1295	m	y			
			1295	m,d	
1288	mw	y			
1265	w	x			CH_2 w, t
1265	m	y			
1238	vvw	y			
			1175	w,sh	

TABLE V-2 (Continued)

Infrared			Raman		Interpretation[d]
Wave Number	Intensity[a] and Polarization[b] (Fig. V-5)		Wave Number	Description[c]	
1208	w	x			CH_2 w, t
1205	m	y			
1161	w	y			
			1155	w,sh	
			1067	m	sk
1064	w	y			
1064	vw	x			
			1045	mw	
931*	m	y			(op) O-H b
			919	vs	sk
918	s	x			
890	m	y			sk
			880	w	
854	vvw	y			CH_2 r
			850	w,sh	
764	w	y			CH_2 r
762	m	x			
693	vvw	y			(op) O=C-OH b
			672	w,d	
664	m	y			

TABLE V-2 (Continued)

Infrared			Raman		Interpretation[d]
Wave Number	Intensity[a] and Polarization[b] (Fig. V-5)		Wave Number	Description[c]	
			592	vw	(op) COOH, sk
586	m	y			
522	w	x,y			
473	m	y			
			438	w	sk
			314	w	sk, H···O st[f]

[a]See footnote a, Table V-1.

[b]The symbols x or y indicate that the band appears with the electric field in the incident radiation parallel to the x-direction or the y-direction, respectively. The x-direction is assumed to be approximately parallel to the crystallographic a-axis, and the y-direction approximately perpendicular to the a-axis. This assumption is based on the dichroism of the lowest frequency CH_2 rocking band.

[c]The following abbreviations are used: s strong, m medium, w weak, v very sh sharp, d diffuse.

[d]See footnote b, Table V-1.

[e]The symbol * indicates that the value given represents the approximate center of a broad or very strong band.

[f]See footnote c, Table V-1.

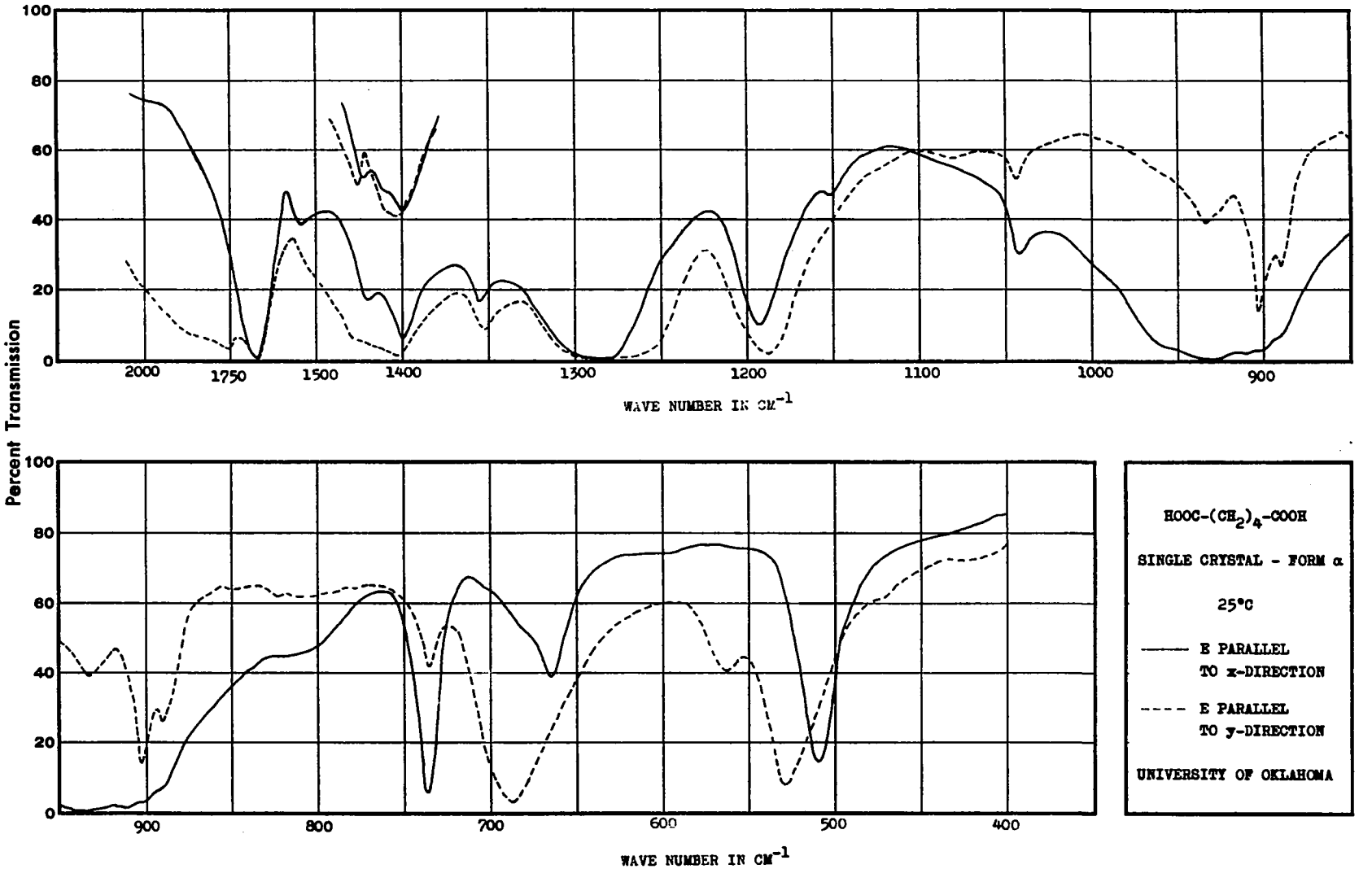


Fig. V-6. Infrared Spectrum of the α-Form of $HOOC(CH_2)_4COOH$; Radiation Incident Normal to $\bar{1}1\bar{1}$-Plane.

TABLE V-3

VIBRATIONAL BANDS OF CRYSTALLINE ADIPIC ACID
$HOOC(CH_2)_4COOH$

Infrared			Raman		Interpretation[d]
Wave Number	Intensity[a] and Polarization[b] (Fig. V-6)		Wave Number	Description[c] (Fig. V-2)	
			2935	vs	a_g, b_g asym. CH_2 st
			2915	vs	
			2896	vs	a_g, b_g sym. CH_2 st
			2866	m	
			2806	s	A_g, B_g 2x(α-CH_2 d)
1765*[e]	m	x			B_u 1193 + 568 = 1761
1679*	s	x,y			a_u, b_u C=O st
			1649	m,d	a_g, b_g
1544*	vw	y			
			1482	w	a_g, b_g CH_2d
1454	m	x			b_u
1447	m	y			a_u
			1446	m	a_g, b_g
1423	m	y			a_u C-O st and (ip)O-H b
1423	s	x			b_u
			1410	s	a_g, b_g α-CH_2d
1408*	s	x			b_u
1400*	s	y			a_u

TABLE V-3 (Continued)

Infrared			Raman		Interpretation[d]
Wave Number	Intensity[a] and Polarization[b] (Fig. V-6)		Wave Number	Description[c] (Fig. V-2)	
			1380	w	a_g, b_g
1355	w	y			b_u
			1352	vw	a_g, b_g
1352	w	x			a_u
			1300	m	a_g, b_g
1288*	vs	y			a_u
1275*	vs	x			b_u
			1247	mw	a_g, b_g
			1220	w	a_g, b_g
1193	s	y			a_u
1188	s	x			b_u
1152	vvw	y			a_u
			1086	m	a_g, b_g
1080*	vvw	x			b_u
			1048	m	a_g
1043	w	x,y			a_u, b_u
934	w	x			b_u
930*	s	y			a_u
			915	s	a_g, b_g
903	s	x,y			a_u, b_u
890	m	x,y			
787[g]	w				a_u,b_u

CH_2 w

C-O st, (ip) O-H b, CH_2 t

CH_2 t

sk

sk

(op) O-H b, CH_2 r, CH_2 t

sk

sk

CH_2 r

TABLE V-3 (Continued)

Infrared			Raman		Interpretation[d]	
Wave Number	Intensity[a] and Polarization[b] (Fig. V-6)		Wave Number	Description[c] (Fig. V-2)		
736	ms	y			b_u	CH_2 r
735	vw	x			a_u	
686	s	x			b_u	(ip) O=C-OH[b]
664	m	y			a_u	
			660	mw	a_g, b_g	
			568	w	a_g, b_g	(op) COOH
561	w	x			a_u	
528	s	x			a_u	
			511	w	a_g, b_g	
510	s	y			b_u	
			298	m,d	a_g, b_g	sk, O···H st[f]

[a]See footnote a, Table V-1.

[b]The radiation was incident normal to the crystallographic $\bar{1}1\bar{1}$ plane. The symbols x or y indicate that the band appears with the electric field mainly parallel to the c-axis or the b-axis, respectively.

[c,d,e,f]See corresponding footnotes in Table V-2.

[g]This band observed by Susi.[85]

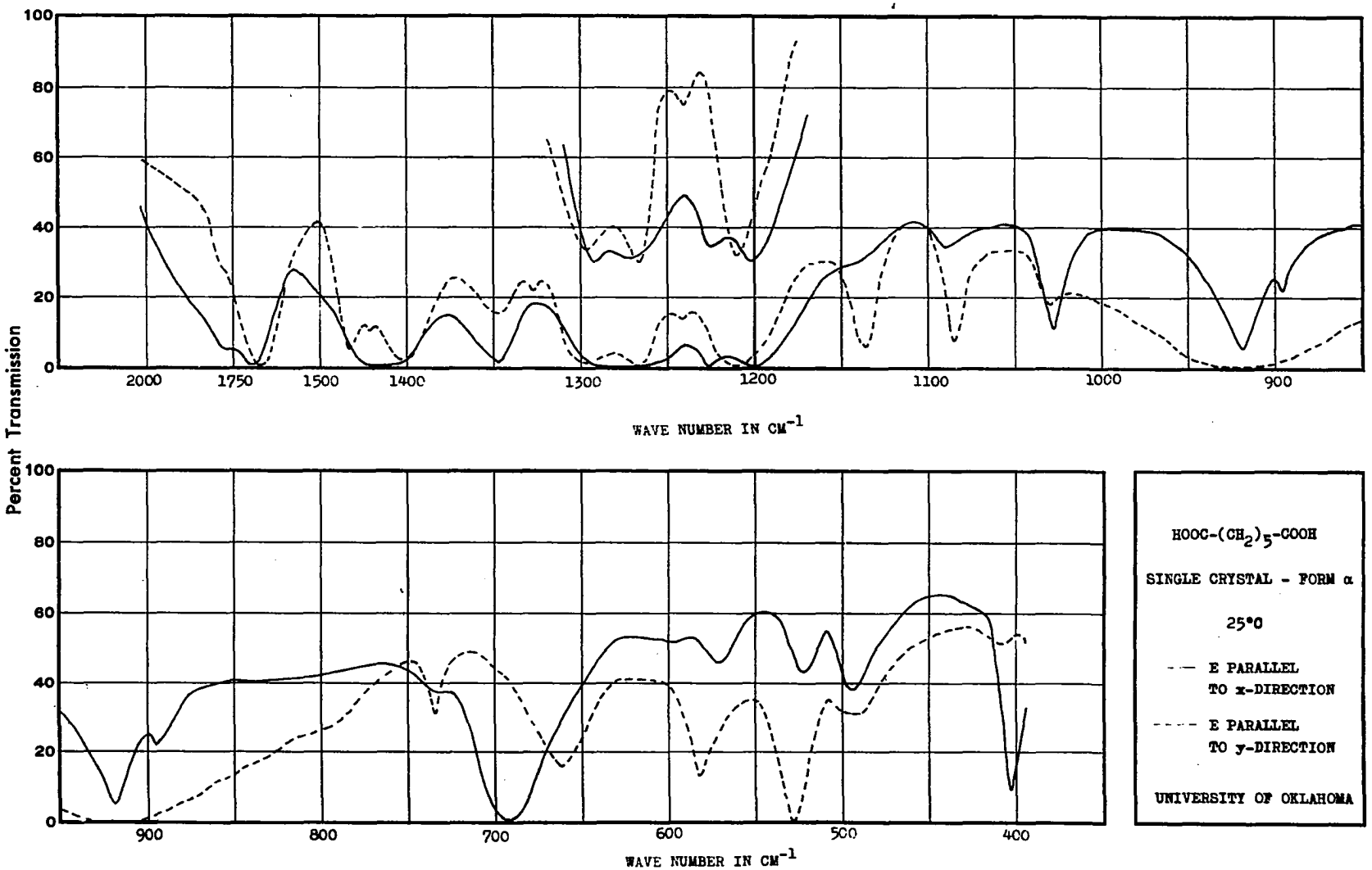


Fig. V-7. Infrared Spectrum of the α-Form of $HOOC(CH_2)_5COOH$; Radiation Incident Normal to the xy-Plane. (See footnote b, Table V-2.)

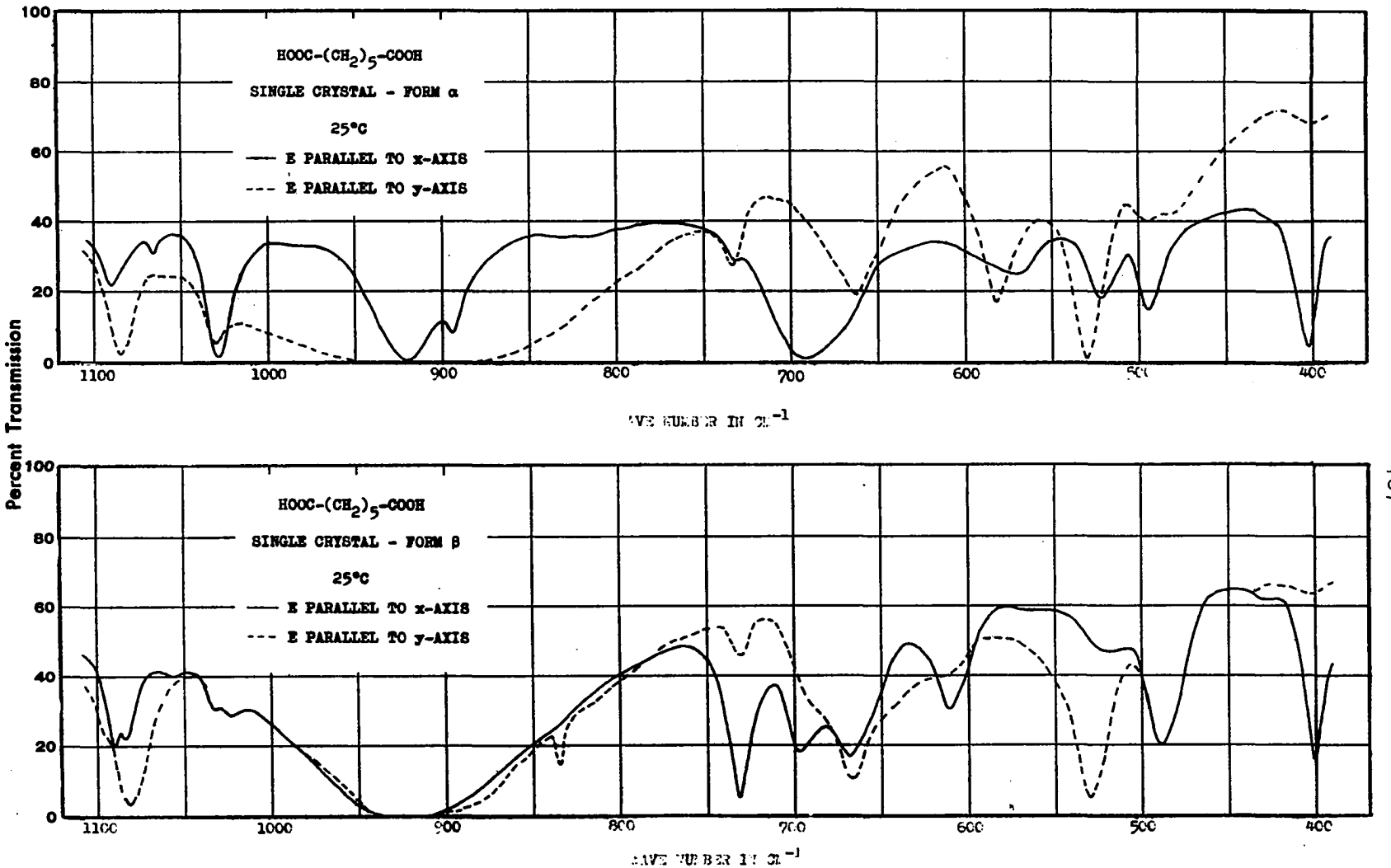


Fig. V-8. Infrared Spectra of the α- and β-Forms of $HOOC(CH_2)_5COOH$; Radiation Incident Normal to the xy-Plane. (See footnote c, Table V-4)

TABLE V-4

VIBRATIONAL BANDS OF CRYSTALLINE PIMELIC ACID
$HOOC(CH_2)_5COOH$

PART A

Infrared

α-Pimelic			β-Pimelic			Interpretation[d]
Wave Number	Intensity[a] and Polarization[b] (Fig. V-7)		Wave Number	Intensity[a] and Polarization[c] (Fig. V-8)		
1770*[e]	m	x	1770*	m	x	899 + 985 = 1794
1695*	vs	x	1690*	vs	x,y	C=O st
1675*	vs	y				
1464*	vs	y	1464*	ms	y	CH_2 d
1443	m	y				C-O st, (ip) O-H b
			1426	s	x	
1402	s	x,y	1404	s	y	α-CH_2 d, w
1347	s	x,y	1347	ms	x	C-O st, CH_2 w
1328	w	y	1331	w	y	
1297*	vs	y	1297	m	y	(ip) O-H b, C-O st, CH_2 w
1291*	vs	x	1294	m	x	
1272*	vs	x	1270	m	x	CH_2 t, w
1267*	vs	y	1268	m	y	
			1246	m	y	
1241	w	y	1241	w	y	
1226*	vs	x	1226	m	x	
1210*	vs	y	1202	m	y	
1202*	vs	x	1200	s	x	
1136	m	y	1140	w	x	sk
			1136	w	y	

TABLE V-4 (Continued)

Infrared						Interpretation[d]
α-Pimelic			β-Pimelic			
Wave Number	Intensity[a] and Polarization[b] (Fig. V-7)		Wave Number	Intensity[a] and Polarization[c] (Fig. V-8)		
1090	w	x	1090	mw	x	sk
			1084	w	x	
1085	m	y				
			1082	m	y	
			1056	vvvw	x	
			1033	vw	x	
1030	mw	y				
1028	w	x	1024	vw	x	
920*	vvs	y	920*	vvs	x,y	(op) O-H b, sk, CH_2 r
919	m	x				
895	w	x				sk
			835	vw	y	
734	vvw	x	732	m	x	CH_2 r
734	vw	y	732	w	y	
693	vs	x	695	mw	x	(ip) O=C-OH b
			669	m	x,y	
662	m	y				
			610	w	x	
594	vvw	x				
582	m	y				(op) C-OH b
570	w	x				
528	s	y	530	s	y	(op) C=O b
522	w	x	522	vm	x	
494	w	x,y	489	m	x,y	(op) O=C-O t, sk
402	s	x	401	s	x	

TABLE V-4 (Continued)

PART B				
Raman				Interpretation[d]
$HOOC(CH_2)_5COOH$		$DOOC(CH_2)_5COOD$		
Wave Number	Description[a] (Fig. V-3)	Wave Number	Description[a]	
2972	s	2972	s	asym. CH_2 st
2947	w	2946	w	2x1472 = 2944
2926	m	2927	m	2x1464 = 2928
2902	vs	2902	vs	sym. CH_2 st
2868	vs	2867	vs	
1644	m,d	1643	m,d	C=O st
1472	w			CH_2 d
1450	s,sh	1450	m,sh	
1406	m,sh	1406	m	α-CH_2 d, w
1315	m	1316	m	(ip) O-H b, C-O st, CH_2 w
1270	m,sh	1270	w	CH_2 t, w
1216	w,d			CH_2 t
1136	w			sk
1086	s,sh	1088	ms	sk
1063	m	1062	mw	sk
1032	m,sh	1032	mw	sk
939	w,sh			(op) O=H b
899	s	870	ms	sk
768	w			CH_2 r (?)
673	w,d	638	vw,d	(ip) O=C-OH b
				D

TABLE V-4 (Continued)

Raman				Interpretation[d]
$HOOC(CH_2)_5COOH$		$DOOC(CH_2)_5COOD$		
Wave Number	Description[a] (Fig. V-3)	Wave Number	Description[a]	
585	w,d			(op) C-OH b
517	w	515	w	(op) C=O b
324	w	323	vw	sk, H···O st[f]
267	w	265	vw	

[a]See footnote a, Table V-1.

[b]The symbols x or y indicate that the band appears with the electric field in the incident radiation parallel to the x-direction or the y-direction, respectively. The x-direction is assumed to be approximately parallel to the crystallographic a-axis, and the y-direction approximately perpendicular to the a-axis. This assumption is based on the dichroism of the lowest frequency CH_2 rocking band in Fig. V-7.

[c]The symbols x and y have the meanings given in footnote b. This assumption is valid only if the crystallographic axes did not change when the crystal under went the α- to β-form transition.

[d,e,f]See corresponding footnotes in Table V-2.

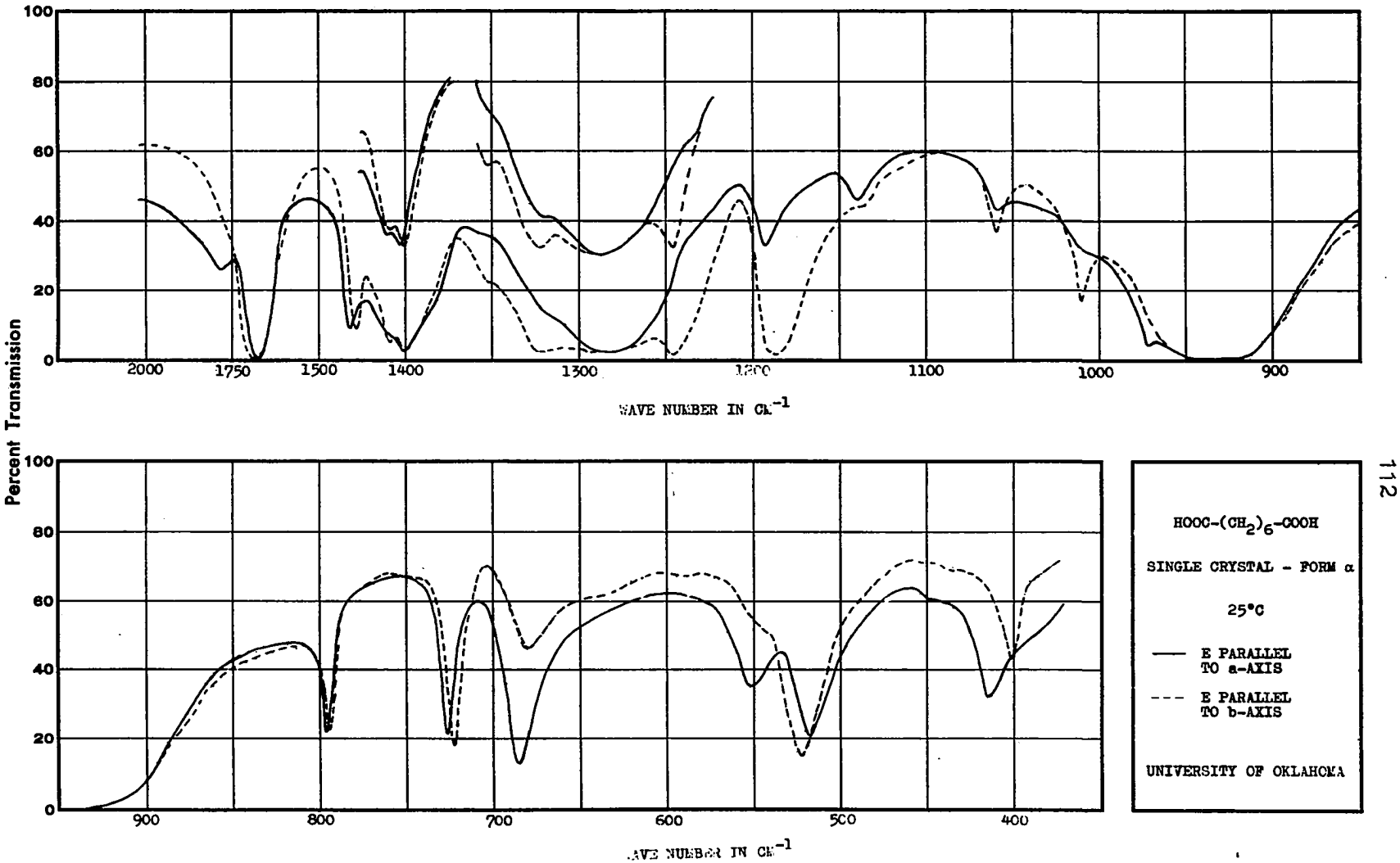


Fig. V-9. Infrared Spectrum of the α-Form of $HOOC(CH_2)_6COOH$; Radiation Incident Normal to the ab-Plane

TABLE V-5

VIBRATIONAL BANDS OF CRYSTALLINE SUBERIC ACID
$HOOC(CH_2)_6COOH$

Infrared			Raman		Interpretation[d]
Wave Number	Intensity[a] and Polarization[b] (Fig. V-9)		Wave Number	Description[c]	
			2949	s	a_g, b_g asym, CH_2 st
			2917	s	
			2896	w	a_g, b_g sym. CH_2 st
			2875	w	
1785*[e]	w	a			B_u
1685*	s	b			a_u C=O st
1665*	s	a			b_u C=O st
			1650	mw,d	a_g, b_g C=O st
1463	m	a			b_u CH_2 d
1458	m	b			a_u CH_2 d
			1458	mw	a_g, b_g CH_2 d
			1433	m	a_g, b_g C-O st, (ip) O-H b
1423	ms	a			b_u C-O st, (ip) O-H b
1420	ms	b			a_u C-O st, (ip) O-H b
			1409	m	a_g, b_g α-CH_2 d
1405	s	a			b_u α-CH_2 d
1403	s	b			a_u α-CH_2 d
1353	w	b			a_u CH_2 w
1324	s	b			a_u CH_2 w
1318*	s	a			b_u CH_2 w

TABLE V-5 (Continued)

Infrared			Raman		Interpretation[d]
Wave Number	Intensity[a] and Polarization[b] (Fig. V-9)		Wave Number	Description[c]	
			1292	m	a_g, b_g } C-O st, (ip) O-H, CH_2 t
1286*	vs	b }			a_u }
1283*	vs	a }			b_u }
1245	ms	b }			a_u } CH_2 t
1235	vvw	a }			b_u }
1193	w	a }			b_u } sk
1187	vs	b }			a_u }
1140	w	a,b			a_u, b_u }
			1097	m	a_g, b_g }
1059	w	a,b			a_u, b_u } sk
			1042	w	a_g, b_g }
			1023	vw	a_g, b_g }
1010	vvw	a }			b_u } sk
1010	mw	b }			a_u }
972	s	a			b_u }
935*	s	a,b			a_u, b_u } (op) O-H b, sk, CH_2 r
			898	m	a_g, b_g }
795	mw	a }			b_u } CH_2 r
794	mw	b }			a_u }
726	m	a }			b_u } CH_2 r
723	m	b }			a_u }
685	m	a }			b_u } (ip) O=C-OH b
680	mw	b }			a_u }

TABLE V-5 (Continued)

Infrared			Raman		Interpretation[d]
Wave Number	Intensity[a] and Polarization[b] (Fig. V-9)		Wave Number	Description[c]	
552	w	a		b_u	(op) C-OH b
552	vvw	b		a_u	
522	m	b		b_u	(op) C=O b
518	m	a		a_u	
415	m	a		b_u	(op) O-C=O t, sk
402	mw	b		a_u	

[a]See footnote a, Table V-1.

[b]The symbols a or b indicate that the band appears with the electric field in the incident radiation parallel to the a-axis or the b-axis, respectively.

[c,d,e]See corresponding footnotes in Table V-2.

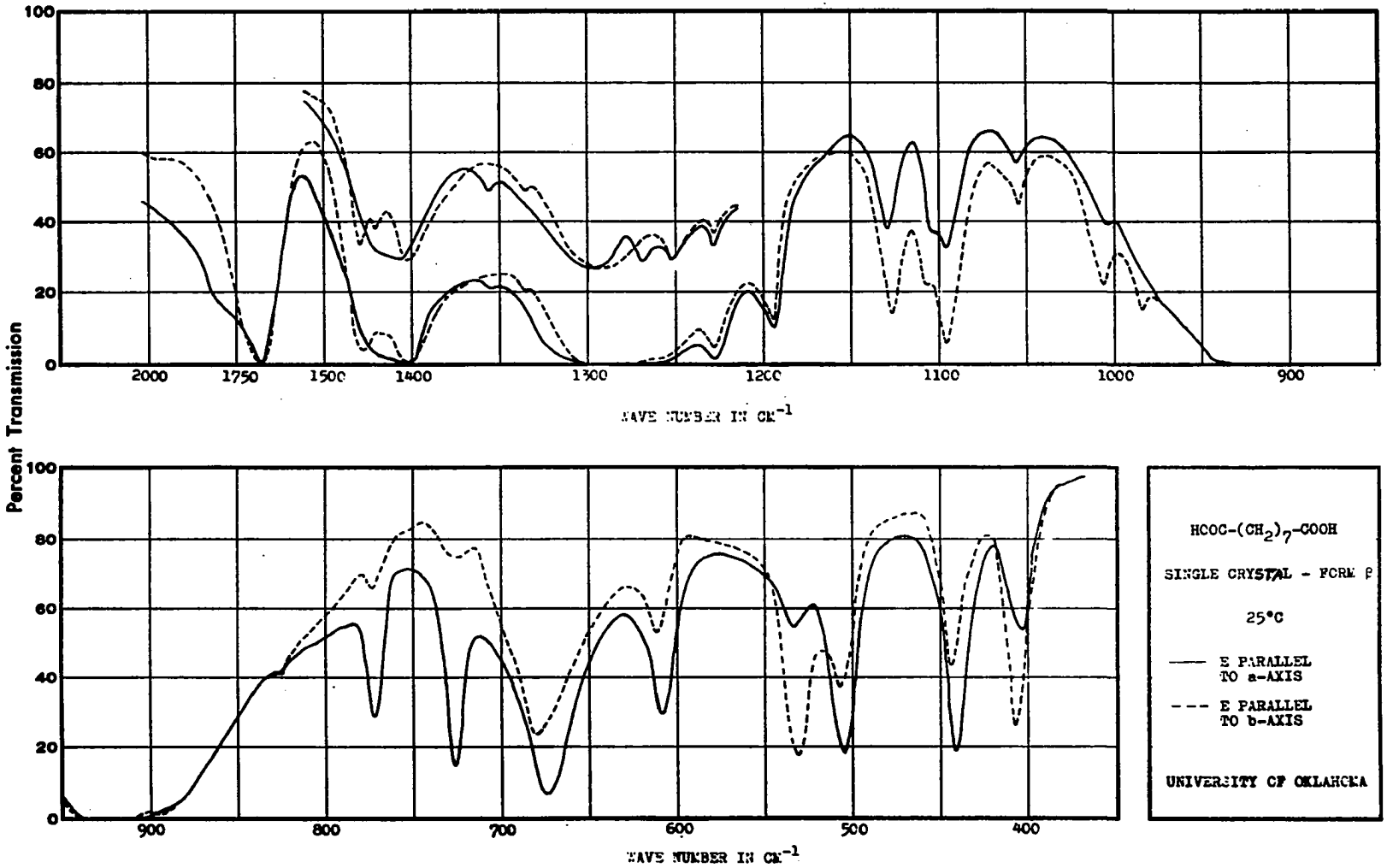


Fig. V-10. Infrared Spectrum of the β-Form of $HOOC(CH_2)_7COOH$; Radiation Incident Normal to the ab-Plane.

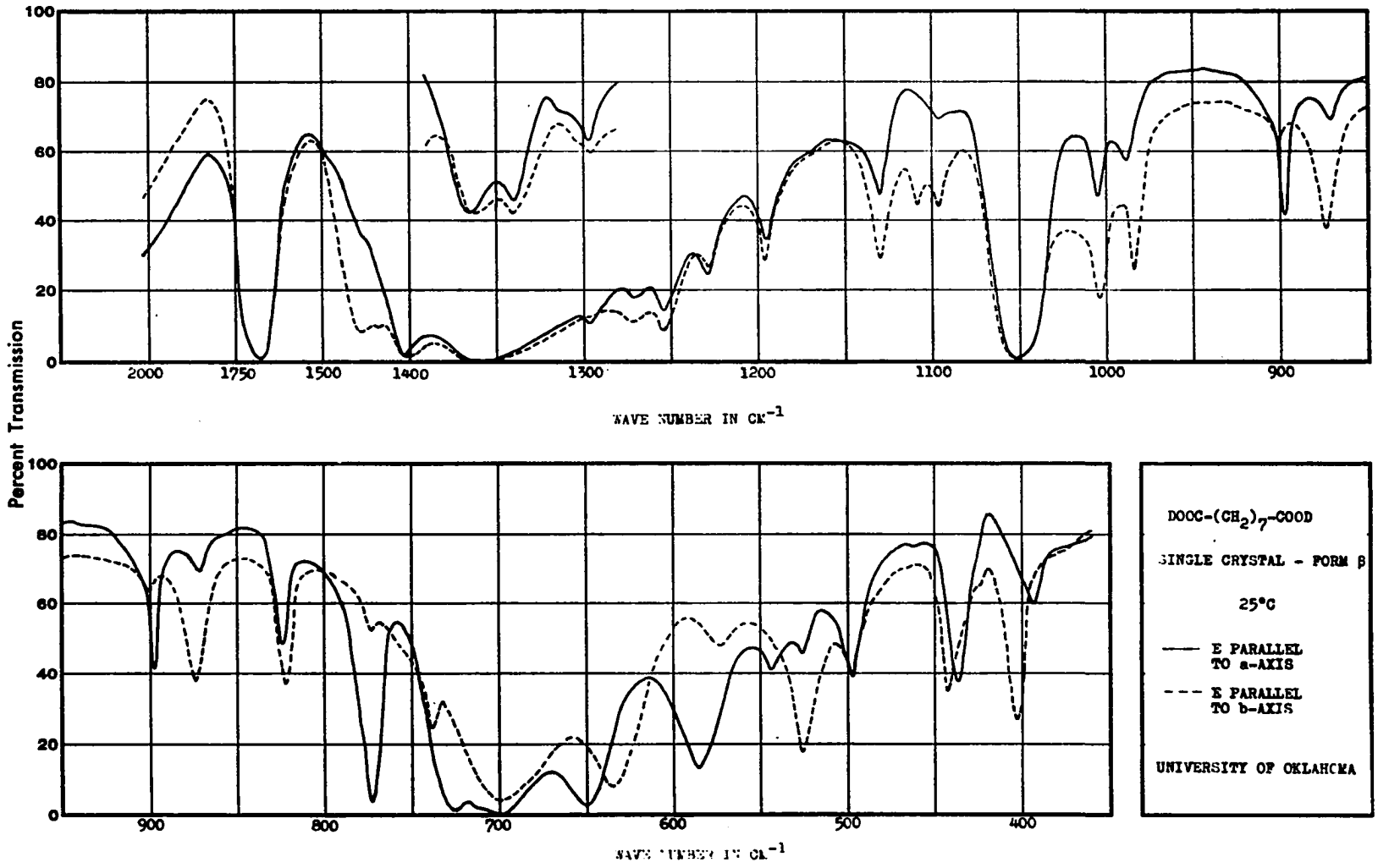


Fig. V-11. Infrared Spectrum of the β-Form of DOOC$(CH_2)_7$COOD; Radiation Incident Normal to the ab-Plane.

TABLE V-6

VIBRATIONAL BANDS OF CRYSTALLINE AZELAIC ACID
PART A: β - $HOOC(CH_2)_7COOH$

Infrared			Raman		Interpretation[d]
Wave Number	Intensity[a] and Polarization[b] (Fig. V-10)		Wave Number	Description[c]	
			2969	m	asym. CH_2 st
			2932	w	2x(CH_2 d)
			2905	vs	sym. CH_2 st
			2882	vs	2x(C-O st)
			2845	s	
1800*[e]	ms	a			
1695*	vs	a,b			C=O st
			1648	w,d	
1458	s	b			CH_2 d
1446*	vs	a			
			1443	w	C-O st, (ip) O-H b
1442*	m	b			
1413	vs	a			α-CH_2 d, w
			1408	w	
1406	vs	b			
1356	w	a			C-O st, CH_2 w
1335	w	b			
1299	vs	a			(ip) O-H b, C-O st, CH_2 w, t
			1296	m,d	
1291	vs	b			

TABLE V-6, PART A (Continued)

Infrared			Raman		Interpretation[d]
Wave Number	Intensity[a] and Polarization[b] (Fig. V-10)		Wave Number	Description[c]	
1269	vs	a			
			1255	m	
1252	s	a,b			CH_2 t, w
1228	s	a,b			
1195	m	b			
1193	m	a			
1129	w	a			
1127	m	b			
			1124	w,sh	
1108	m	b			
1103	w	a			
1096	m	a			
1096	s	b			sk
			1065	m	
1055	w	a			
1054	w	b			
1006	w	b			
1005	vw	a			
985	w	b,(a?)			
925*	vvs	a,b			
			902	mw	(op) O-H b, sk, CH_2 r
826	vvw	a			
826	vvw	b			CH_2 r, sk

TABLE V-6, PART A (Continued)

Infrared			Raman		Interpretation[d]
Wave Number	Intensity[a] and Polarization[b] (Fig. V-10)		Wave Number	Description[c]	
773	vw	b			CH_2 r
772	m	a			
727	ms	a			CH_2 r
726	vvw	b			
681	m	b			(ip) O=C-OH b
676	s	a			
612	w	b			
609	mw	a			
534	w	a			(op) C-OH b
531	m	b			
508	w	b			
504	m	a			
444	m	b			(op) C=O b
442	ms	a			
407	m	b			(op) O-C=O t, sk
402	w	a			

PART B: β-DOOC$(CH_2)_7$COOD

Wave Number	Intensity[a] and Polarization[b] (Fig. V-11)		
1685*	vs	a,b	C=O st
1457	s	b	CH_2 d
1435	ms	b	C-O st, α-sk

TABLE V-6, PART B (Continued)

Infrared Wave Number	Intensity[a] and Polarization[b] (Fig. V-11)		Interpretation[d]
1411*	vs	a	α-CH_2 d, w
1406*	vs	b	
1366	vs	a	C-O st, (CH_2 w)
1362	vs	b	
1340	s	a,b	
1297	ms	a,b	C-O st, (CH_2 w)
1272	m	a,b	
1255	m	a,b	CH_2 t, w
1229	mw	a	
1228	mw	b	
1196	mw	b	
1195	mw	a	
1130	mw	a,b	sk
1109	w	b	
1096	vw	a	
1096	w	b	
1053	vs	a,b	(ip) O-D b
1004	m	a	sk
1004	w	b	
988	w	a	
984	m	b	
901	w	b	CH_2 r
897	mw	a	

TABLE V-6, PART B (Continued)

Infrared Wave Number	Intensity[a] and Polarization[f] (Fig. V-11)		Interpretation[d]
873	mw	b	sk
871	vw	a	
824	mw	a	CH_2 r
821	mw	b	sk
773	vs	a	CH_2 r
773	vvw	b	
728	vw	b	CH_2 r
726	vs	a	
698*	vs	a,b	(op) O-D b
650	s	a	(ip) O=C-OD b
635	s	b	
585	ms	a	
572	w	b	
543	w	a	(op) C-OD b
526	vvw	a	
526	m	b	
497	w	a,b	
443	m	b	(op) C=O b
436	m	a	
402	m	b	(op) O-C=O t, sk
393	w	a	

a,b,c,d,e See corresponding footnotes in Table V-5.

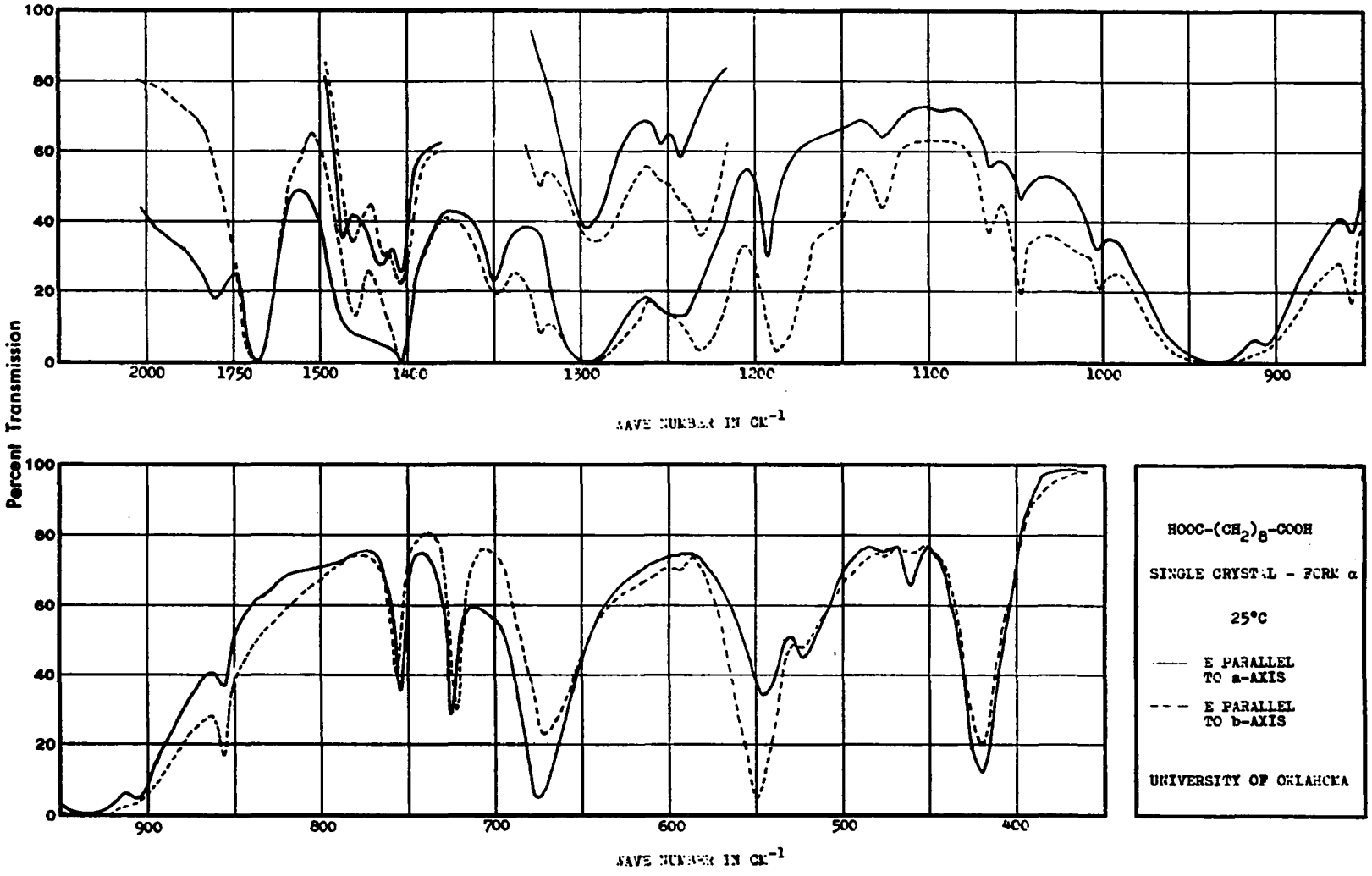


Fig. V-12. Infrared Spectrum of the α-Form of $HOOC(CH_2)_8COOH$;

Radiation Incident Normal to the ab-Plane.

TABLE V-7

VIBRATIONAL BANDS OF CRYSTALLINE SEBACIC ACID
$HOOC(CH_2)_8COOH$

Infrared			Raman		Interpretation[d]
Wave Number	Intensity[a] and Polarization[b] (Fig. V-12)		Wave Number	Description[c] (Fig. V-4)	
			2937	s	a_g, b_g 2x(CH_2 d)
			2911	vs	a_g, b_g asym. CH_2 st
			2889	vs	a_g, b_g
			2871	s	a_g, b_g sym. CH_2 st
			2850	s	a_g, b_g 2x(C-O st)
			2783	w	A_g 2x1408 = 2816 (?)
			2730	w	A_g 1297 + 1430 = 2707 (?)
1804*[e]	m	a			B_u 806 + 1297 = 1803 (?)
1685*	s	a,b			a_u, b_u C=O st
			1643	w,d	a_g, b_g
1470	m	a			b_u
			1468	mw	a_g, b_g CH_2 d
1466	m	b			a_u
			1434	m	a_g, b_g
1430	ms	a			b_u C-O st, (ip) O-H b, CH_2 w
1426	ms	b			a_u
			1411	m	a_g, b_g
1408	s	a,b			a_u, b_u α-CH_2 d
			1373	w	a_g, b_g
1350	m	a			b_u CH_2 w
1348	m	b			a_u

TABLE V-7 (Continued)

Infrared					Interpretation[d]
Wave Number	Intensity[a] and Polarization[b] (Fig. V-12)		Wave Number	Description[c] (Fig. V-4)	
1325	w	b		a_u	CH_2 w
			1298	m a_g, b_g	C-O st, (ip) O-H b, CH_2 t
1297	s	a		b_u	
1293	s	b		a_u	
			1278	mw a_g, b_g	CH_2 t
1256	m	a		b_u	
1256	w	b		a_u	
1245	m	a		b_u	
1245	w	b		a_u	
1231	s	b		a_u	sk, CH_2 t, r
			1214	w a_g, b_g	
1192	m	a		b_u	
1185	s	b		a_u	
1127	vvw	a		b_u	sk
1127	vw	b		a_u	
			1103	s a_g, b_g	
			1065	m a_g, b_g	
1065	vvw	a		b_u	
1065	vw	b		a_u	
			1049	w a_g, b_g	
1047	vw	a		b_u	
1047	w	b		a_u	
1003	vw	a		b_u	CH_2 r
1002	vw	b		a_u	

TABLE V-7 (Continued)

Infrared			Raman		Interpretation[d]
Wave Number	Intensity[a] and Polarization[b] (Fig. V-12)		Wave Number	Description[c] (Fig. V-4)	
932*	vs	a,b		a_u, b_u	(ip) O-H b, sk
			909	m a_g, b_g	
906	m	a,b		a_u, b_u	
			893	w a_g, b_g	
856	w	b		a_u	CH_2 r
855	vw	a		b_u	
756	mw	b		a_u	CH_2 r
754	mw	a		b_u	
725	m	a		b_u	CH_2 r
722	m	b		a_u	
675	s	a		b_u	(ip) O=C-OH b
672	m	b		a_u	
			672	w a_g, b_g	
550	s	b		a_u	(op) C-OH b
546	m	a		b_u	
522	vw	a,b		a_u, b_u	(op) C=O b
			506	w a_g, b_g	
461	vw	a		b_u	(op) O-C=O t, sk
419	ms	a,b		a_u, b_u	

a,b,c,d,e See corresponding footnotes in Table V-5.

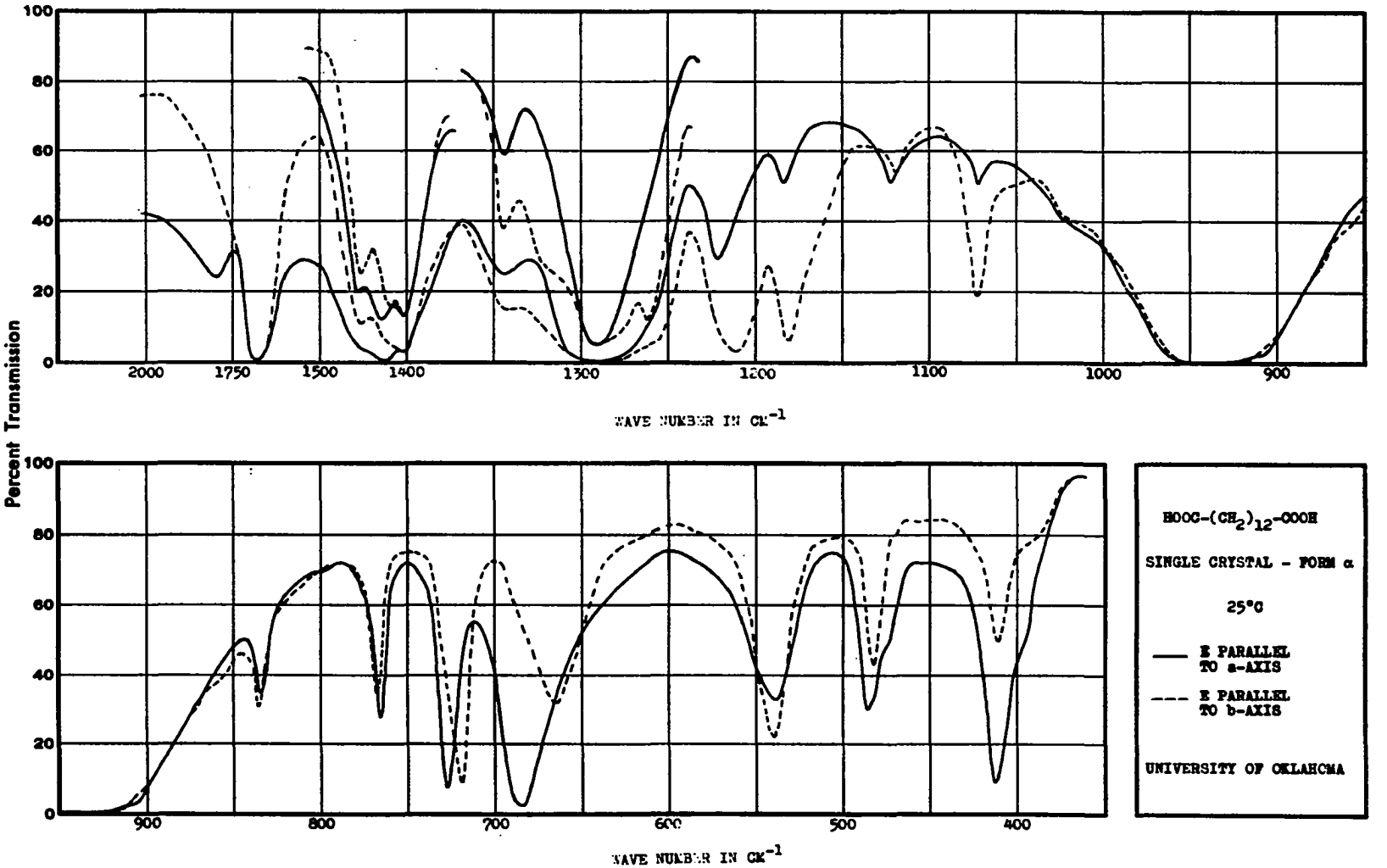


Fig. V-13. Infrared Spectrum of the α-Form of $HOOC(CH_2)_{12}COOH$; Radiation Incident Normal to the ab-Plane.

TABLE V-8

VIBRATIONAL BANDS OF CRYSTALLINE TETRADECANEDIOIC ACID
$HOOC(CH_2)_{12}COOH$

Infrared			Raman		Interpretation[d]	
Wave Number	Intensity[a] and Polarization[b] (Fig. V-13)		Wave Number	Description[c]		
			2935	w,d	A_g	2x1466 = 2932
			2912	w	A_g	2x1459 = 2918
			2878	s	a_g, b_g	asym. CH_2 st
			2842	s	a_g, b_g	sym. CH_2 st
			2783	w	A_g	2x1404 = 2808
			2718	w	A_g, B_g	1289 + 1428 = 2717
1794*[e]	w	a			B_u	
1676*	s	a,b			a_u, b_u	C=O st
			1643	vvw,d	a_g, b_g	C=O st
			1466	w	a_g, b_g	CH_2 d
1459	ms	a			b_u	CH_2 d
1454	m	b			a_u	CH_2 d
			1430	m	a_g, b_g	C-O st, (ip) O-H b
1428	m	a			b_u	C-O st, (ip) O-H b
1423	m	b			a_u	C-O st, (ip) O-H b
			1411	vvw	a_g, b_g	α-CH_2 d
1404	ms	a,b			a_u, b_u	α-CH_2 d
1344	m	a,b			a_u, b_u	CH_2 w
1321	m	b			a_u	CH_2 w
			1298	m	a_g, b_g	C-O st, (ip) O-H b, CH_2 t
1289	s	a,b			a_u, b_u	C-O st, (ip) O-H b, CH_2 t
			1282	vvw	a_g, b_g	C-O st, (ip) O-H b, CH_2 t

TABLE V-8 (Continued)

Infrared			Raman		Interpretation[d]
Wave Number	Intensity[a] and Polarization[b] (Fig. V-13)		Wave Number	Description[c]	
1262	m	b			a_u
			1247	vw	a_g, b_g
1221	mw	a			b_u
1211	s	b			a_u
1183	w	a			b_u
1181	m	b			a_u
1122	w	a			b_u
1119	w	b			a_u
			1112	w	a_g, b_g
1073	w	a			b_u
1073	m	b			a_u
			1064	w	a_g, b_g
1020	vw	a,b			a_u, b_u
935*	vs	a,b			a_u, b_u
			902	vvw	a_g, b_g
835	w	b			a_u
833	w	a			b_u
767	mw	b			a_u
765	m	a			b_u
727	ms	a			b_u
719	ms	b			a_u
685	s	a			b_u
664	m	b			a_u

Interpretation[d]
CH_2 w, t
sk
CH_2 t, r
sk
(op) O-H b, sk, CH_2 r
CH_2 r
CH_2 r
CH_2 r
(ip) O=C-OH b

TABLE V-8 (Continued)

Infrared			Raman		Interpretation[d]
Wave Number	Intensity[a] and Polarization[b] (Fig. V-13)		Wave Number	Description[c]	
540	m	b		a_u	(op) C-OH b
538	m	a		b_u	
486	m	b		a_u	(op) C=O b
482	mw	a		b_u	
473	w	a			
412	s	a		b_u	(op) O-C=O t, sk
410	mw	b		a_u	

a,b,c,d,e See corresponding footnotes in Table V-5.

CHAPTER VI

INTERPRETATION OF OBSERVED SPECTRA

Introduction

The even dicarboxylic acids apparently crystallize only in one polymorph, the α-form, with the symmetry of space group C_{2h}^5. A single vibrational unit cell analysis should therefore account for the observed vibrational spectra of adipic, suberic, sebacic, and tetradecanedioic acids. Succinic acid, however, is an exception, crystallizing in both α- and β-forms. Assuming that the sample used to obtain the Raman spectrum of succinic acid was the α-form, the polymorph stable at room temperature with symmetry C_{2h}^5, the analysis should also account for this spectrum.

With what symmetry the odd dicarboxylic acids crystallize is not as clear, as can be seen in Table IV-1. It would appear that the α-form of the odd acids have the space group C_{2h}^6. The space group of the β-form is apparently not the same for all the odd acids. However, there may be errors in some of the early x-ray diffraction reports. The one crystal used in this study known with certainty to be a β-form was of azelaic acid. This crystal was shown by van der Helm to have the symmetry of C_{2h}^5. The differences between space groups C_{2h}^5 and C_{2h}^6 are as follows: C_{2h}^5 possesses two-fold screw axes and its translation group is $\Gamma_m(2\tau_x;2\tau_y;2\tau_z)$, whereas C_{2h}^6 possesses ordinary two-fold axes and

has the translation group $\Gamma_m(2\tau_x; \tau_y, \tau_z; \tau_y, -\tau_z)$.[112] Hence there will be no essential difference in the assignment of the vibrations to symmetry species. However, the dichroism of the infrared bands could be different for the α- and β-form of the odd acids.

There are 3n-6 normal vibrations for a "free" molecule composed of n atoms. The molecule in a crystal is not free and hence there occur also "external" rotational and translational vibrations. These external vibrations are due primarily to the action of van der Waals' forces between molecules in the crystal. The frequencies associated with such vibrations are expected to lie below the frequency range of the present study ($< 200\ cm^{-1}$). Lattice vibrations arising from the action of hydrogen bonding should be of somewhat higher frequency. This study is primarily concerned with the internal vibrations. If there are N molecules per unit cell and n atoms per molecule, there are Nx(3n-6) unit cell fundamentals of the internal type.

Even Acids

The monoclinic unit cell of the α-form of the even acids is given in Chapter IV. There are two molecules per unit cell. The two shorter axes are orthogonal and have been designated by the letters a and b, the a-axis being the longer axis (except for α-succinic acid). The methylene chains are approximately parallel to the c-axis, which is also perpendicular to the b-axis and makes an angle β with the a-axis.

The unit cell of space group C_{2h}^5 possesses eight inversion centers, two glide planes, and four two-fold screw-axes.[112] Each of the two even-acid molecules in the unit cell possesses the symmetry C_i.

If an analysis is made on the basis of the molecular symmetry C_i

one finds vibrations of species a_g and a_u. The presence of two molecules in the unit cell causes the vibrations of species a_g to double into an equal number of vibrations of species a_g and b_g. Similarly, for each vibration of species a_u in the molecule there will be a pair of vibrations of species a_u and b_u, respectively. Vibrations of species a_u and b_u are active in infrared absorption but not Raman-active, whereas vibrations of species a_g and b_g are active only in the Raman effect. However, it is expected that there will be a number of near coincidences in frequency between infrared and Raman bands.

The infrared-active fundamentals which are symmetric or antisymmetric with respect to a screw rotation belong to species a_u and b_u, respectively. The Raman-active fundamentals symmetric or antisymmetric to a screw rotation belong to species a_g and b_g, respectively. The motions of the two molecules in a unit cell are in-phase for a_u and a_g and out-of-phase for b_u and b_g. For each even acid there are an equal number of fundamental vibrations of each of the species a_u, b_u, a_g, and b_g.

From Table IV-1 we note that the planes of the COOH groups are tilted approximately 11° out of the skeletal plane for succinic acid, and approximately 3° for sebacic acid. Hence to a fair approximation the vibrations of the even acids may be classed according to whether they are parallel to or perpendicular to the skeletal plane (in-plane or out-of-plane). This has been done in the infrared analysis of adipic acid by Susi. However, since the planes of the two molecules in the unit cell are not parallel, the resultant dipole moment change due to a vibration will not in general be parallel or perpendicular to the plane of a given molecule. The a_u and b_u vibrations can be polarized either along the

b-axis or perpendicular to the b-axis. The out-of-plane vibrations should be approximately perpendicular to the c-axis of the crystal. Thus, corresponding to an out-of-plane a_u vibration of a single molecule we may expept an a_u band polarized along the b-axis and a b_u band polarized perpendicular to both the b-and c-axes with a component along the a-axis. In-plane a_u vibrations of a single molecule also give rise to a_u, b_u doublets for the crystal. The a_u component is polarized in the b-direction, whereas the polarization of the b_u component will depend upon the nature of the vibration.

All of the infrared spectra of the even acids except adipic acid were obtained with the polarized radiation incident normal to the ab-plane of the crystals with the electric vector parallel first to the a-axis and then to the b-axis. The absorption bands observed in the full curves represent essentially b_u vibrations, and the bands in the dashed curves represent a_u vibrations. The adipic acid spectra appear different from those of the other acids, as will be explained later, and should show bands polarized along the c-axis with a small a-component and bands perpendicular to the c-axis with a b-component (primarily a_u out-of-plane vibrations).

For the four COOH groups we should expect thirty-six vibrations, nine each of the four species. These may be classed roughly as in- and out-of-plane modes. The in-plane modes being C=O, C-O, O-H stretching, and planar O=C-O, COH angle deformations; the out-of-plane modes being C=O, C-O, O-H, O=C-O non-planar bending. These vibrations should remain fairly constant in frequency, independently of chain length. The number of vibrations associated with the methylene chain, of course,

will increase with chain length. The classification of the internal vibrations is summarized for the even acids in Table VI-1.

The selection rules for binary combination and overtone bands are as follows:

$$a_g \times a_g = A_g \qquad b_g \times b_g = A_g$$
$$a_u \times a_u = A_g \qquad b_u \times b_u = A_g$$
$$a_u \times a_g = A_u \qquad b_u \times b_g = A_u$$
$$a_u \times b_u = B_g \qquad a_g \times b_g = B_g$$
$$a_g \times b_u = B_u \qquad a_u \times b_g = B_u$$

It is seen that overtones can occur only in the Raman spectrum and that binary combinations occurring in the infrared spectrum must be composed of an infrared- and a Raman-active fundamental.

In examining the infrared spectra of the even acids it may not always be possible to resolve the a_u and b_u components of a particular fundamental motion. The difference in frequency between a_u and b_u components, or the "splitting", depends on the strength of the interaction between adjacent molecules. This interaction depends on the crystal form and the distance between interacting atomic groups. In the even acids where the skeletal planes are not parallel to one another the a_u and b_u components possess polarizations which are nearly at right angles. This aids in resolving a_u, b_u doublets. However, if the splitting is small, particularly if the absorption is appreciable, it is quite possible that the a_u and b_u frequencies will appear unresolved. For the most part the splittings in the even acids have been found to be less than 10 cm^{-1}.

It is highly unlikely that a_g and b_g doublets have been resolved in the Raman spectra obtained of the even acids. While such splittings

TABLE VI-1

VIBRATIONAL SPECIES OF EVEN DICARBOXYLIC ACIDS
$HOOC(CH_2)_nCOOH$, n = 0,2,4,···

Vibrations	Unit Cell Species	Infrared a_u	Polarization[a] b_u
Methylene Group	$3n(a_u + b_u + a_g + b_g)$		
sym. CH_2 stretching	$(n/2)(a_u + b_u + a_g + b_g)$	b	$\perp b, \perp c$
asym. CH_2 stretching	same	b	$\perp b, \perp c$
CH_2 deformation	same	b	$\perp b, \perp c$
CH_2 wagging	same	(b)*	c
CH_2 twisting	same	(b)*	$(\perp b, \perp c)$*
CH_2 rocking	same	b	$\perp b, \perp c$
Skeletal[b]	$(3n/2)(a_u + b_u + a_g + b_g)$		
in-plane	$n(a_u + b_u) + (n + 1)(a_g + b_g)$	(b)* or (b)*	c or $(\perp b, \perp c)$*
out-of-plane	$(n/2)(a_u + b_u) + [(n - 2)/2](a_g + b_g)$	b	$\perp b, \perp c$
COOH Group	$9(a_u + b_u + a_g + b_g)$		
<u>in-plane</u>			
C=O stretching	$a_u + b_u + a_g + b_g$	b	$\perp b$
C-O stretching	same	b	$\perp b$
O-H stretching	same	b	$\perp b$
O-H bending	same	b	$\perp b$
O-C=O angle bending	same	b	$\perp b$
<u>out-of-plane</u>			
C=O bending	same	b	$\perp b, \perp c$
C-O bending	same	b	$\perp b, \perp c$

TABLE VI-1 (Continued)

Vibrations	Unit Cell Species	Infrared Polarization[a]	
		a_u	b_u
O-H bending	same	b	$\perp$b, $\perp$c
O-C=O torsion	same	b	$\perp$b, $\perp$c
TOTAL	$[(9n + 18)/2]\ (a_u + b_u + a_g + b_g)$		

[a]The symbols b or c indicate that the band should appear with the electric field in the incident polarized radiation parallel to the b-axis or c-axis, respectively. The symbols $\perp$b and $\perp$b, $\perp$c indicate that the band should appear with the electric field in the incident radiation polarized perpendicular to the b-axis and the b- and c-axes, respectively. The symbol ()* indicates that the band is essentially forbidden and should appear only weakly, if at all.

[b]In enumerating the skeletal vibrations three translations and three rotations have been subtracted. This ignores certain low frequency vibrations.

should occur also in the Raman spectra, none appears to have been reported. It may be either that the splittings are small or that one of the components is much weaker than the other, thus making its detection difficult.

The spectra of the even acids are shown in Figures V-1, 2, 4, 6, 9, 12, 13. The vibrational bands are listed and interpreted in Tables V-1, 3, 5, 7, 8. The crystals of suberic, sebacic, and tetradecanedioic acids were of the same form and habit, hence their spectra are very similar. The adipic acid crystal was of the same form as the others, but of a different habit. Hence the polarizations of the bands observed for adipic acid appear different from those of the other acids. It is convenient to discuss the spectra of all the even acids together.

Carboxyl Group Bands

The carboxyl group bands constitute the most prominent features in the infrared spectra of the dicarboxylic acids. These highly polar groups affect the electrical properties of the adjacent methylene groups (α-CH_2) and couple mechanically with the vibrating skeletal chain. The mixing of chain and carboxyl group vibrations will depend upon their frequencies and symmetries. There is evidence that such mixing can affect both the intensities and possibly the polarization of the methylene chain modes.[60]

The carboxyl bands cause heavy infrared absorption in the regions from 1700 to 1250 cm^{-1}, 1000 to 950 cm^{-1}, and near 690 cm^{-1}. (See Table IV-3.) The strength of these bands, due to the thickness of the crystals, made it difficult to obtain useful dichroism data.

In the monomer, carboxylic acids show a strong band in the 1750 cm^{-1} region due to C=O stretching. However, hydrogen bonding such as

occurs in the dimeric and higher polymeric forms causes the C=O stretching band to be lowered to the 1690-1650 cm^{-1} region. In all of the acids studied a strong infrared band was found near 1690 cm^{-1} with both a- and b-polarized components. Only for suberic acid was this doublet resolved into two distinct bands, but it can be assumed to be an a_u, b_u doublet for all the acids. The corresponding a_g and b_g bands were found near 1650 cm^{-1} in the Raman spectra but were not resolved. The observed Raman bands are rather diffuse and the intensity decreased with increasing chain length.

A broad shoulder on the C=O stretching band, polarized in the a direction, was found to occur at approximately 1750 cm^{-1}. This band has been interpreted as a sum band of an infrared skeletal and a Raman COOH fundamental. Since the Raman spectra obtained were not consistently good throughout the whole series, it is not possible to offer an interpretation of this band for all of the acids.

Bands occurring near 1300 cm^{-1} and 1430 cm^{-1} in the infrared spectrum of carboxylic acids have been empirically assigned to a mixture of C-O and O-H stretching vibrations,[85,101] Holland has shown for stearic acid that the 1438 cm^{-1} vibration deviates from the C-O bond direction and has concluded that the band probably involves an appreciable mixture of O-H stretching.

A recent normal coordinate analysis of the dimeric form of acetic acid, $(CH_3COOH)_2$, showed that the infrared band occurring near 1424 cm^{-1} is due to C-O stretching coupled with C-C stretching, and possibly slightly coupled to in-plane OH bending.[113] However, the corresponding Raman band, predicted to occur near 1447 cm^{-1}, is due to C-O stretching coupled with

in-plane OH bending. The infrared-active bands observed at 1294 cm^{-1} in the infrared and at 1255 cm^{-1} in the Raman spectrum were shown to be due to in-plane OH bending coupled with C-O stretching. While the acetic acid dimer is very different from the dibasic acids, this information is useful in assigning the COOH modes.

In most of the spectra of these acids the 1430 cm^{-1} band was resolved into an a_u, b_u doublet. The band at 1300 cm^{-1} was extremely strong, but could be seen to be composed of a- and b-polarized components, indicative of an a_u, b_u doublet. Medium intensity bands in the Raman spectra of these acids occur near both 1430 cm^{-1} and 1300 cm^{-1}. However the relative intensity of these bands slightly increased with chain length, contrary to the decrease in intensity of the C=O stretching Raman band. Raman bands corresponding to methylene deformation and methylene wagging modes, respectively, occur near these frequencies for the long-chain n-paraffins. Hence it is likely that, as the chain length increases in the dibasic acids, there is some overlapping between methylene deformation and wagging and the coupled C-O stretching and in-plane OH bending vibrations in the bands occurring at 1430 cm^{-1} and 1300 cm^{-1}. This would account for the fact that the intensity of these Raman bands increases with chain length.

The only information concerning the infrared COOH bands in the 1000-950 cm^{-1} region must be obtained primarily from the spectrum of adipic acid. The bands observed in this spectrum, Fig. V-6, are polarized mainly parallel to the chain axis with a large a-component and mainly parallel to the b-axis with a slight a-component, respectively. Two weak bands (934 and 890 cm^{-1}) observed in the dotted curve probably

are a-components. The weak band at 934 cm^{-1} is probably the b_u out-of-plane OH bending mode. The weak band at 890 cm^{-1} could be a B_u combination band. The medium band at 903 cm^{-1} in this curve has been assigned as a terminal skeletal stretching mode. A similar band has been observed for the n-paraffins. The full curve, representing the absorption when the electric vector in the incident radiation is approximately in the b-direction, shows strong bands due to an overlapping of out-of-plane a_u bands arising from methylene rocking-twisting, and out-of-plane OH bending.

Raman bands are found in this region which decrease in relative intensity and slightly in frequency as the chain length increases. This probably reflects the lessening of importance of the out-of-plane OH bending vibration and the increasing importance of methylene chain vibrations in determining the Raman spectrum.

Near 685 cm^{-1} an a_u, b_u doublet is found which has been assigned to in-plane O=C-O bending.[60,100] The b_u-component of this doublet was found in all cases to be more intense than the a_u-component. A weak Raman band, probably an unresolved a_g, b_g doublet, has been found near this frequency and probably also arises from O=C-O bending. That this band has not been observed in the Raman spectra of suberic and tetradecanedioic acids can be attributed to their inferior quality.

To help in the interpretation of the bands below 700 cm^{-1}, the polarized infrared spectra have been obtained for the normal alcohol and the monocarboxylic acid with twelve methylene groups. (See Appendix III). These data, when compared with the infrared data obtained on tetradecanedioic acid, can help establish which vibrations might be due to skeletal modes in the 700 to 400 cm^{-1} region. Three bands are observed near 540,

490 and 400 cm^{-1} in both the mono- and dibasic acids. The intensity of the bands for the monocarboxylic acid is about one-half that of the dibasic acid. A comparison of the rocking bands in these two curves and in Holland's curves for stearic and palmitic acids indicates that the dibasic acid crystal is only slightly thicker than the monobasic crystal. The difference in thickness is not sufficient, however, to explain the intensity difference in these bands. It may also be noted that the bands are similar in their polarization characteristics. The infrared spectrum of 1-tetradecanol, $CH_3(CH_2)_{12}CH_2OH$, does not exhibit these bands. To check the possibility that the alcohol crystal was too thin to show these bands, crystals were stacked to form a thick sample and a non-polarized spectrum was obtained from 600 to 400 cm^{-1}. At most a slight indication of a band occurs near 418 cm^{-1} where there is an atmospheric band which is difficult to eliminate even by flushing the spectrometer with dry nitrogen. It would appear, therefore, that these bands are due to the COOH end groups. This would account for the decrease in intensity of these bands in the monobasic acid and their absence in the spectrum of the normal alcohol.

Tentatively these bands have been assigned to out-of-plane vibrations, of C-O, C=O and O=C-O, respectively. It is likely that some interaction takes place between the out-of-plane motions of the COOH-group and the out-of-plane rocking and bending of the carbon skeleton. Such mixing should become more apparent with shorter chain length. These bands are observable for sebacic and suberic acids, but their character and frequencies are changed slightly. The shape and polarization of the bands could well be affected by the carboxyl plane tilt, which becomes larger the shorter the chain. In the sample of adipic acid only the two

higher frequency bands are present and the lower frequency band was not noted. The absence of the band near 400 cm^{-1} in adipic acid certainly causes speculation concerning its assignment as a COOH band. Further investigation is needed to settle this matter. However, the assignment of the two higher bands as COOH modes is more substantially based.

Raman bands have been noted in this region only in the better spectra of adipic, pimelic and sebacic acids. It is likely that these bands have a similar origin.

Methylene and Hydroxyl Stretching Vibrations

In the Raman spectra of all the acids there are numerous bands in the 3000 to 2700 cm^{-1} region. Some of these bands, particularly those of higher frequencies, are among the strongest bands observed. For succinic acid four bands were found, for sebacic acid seven bands. The fundamentals in this region should increase in number with the chain length, and generally this has been observed. The fact that fewer bands have been observed in this region for tetradecanedioic acid than for sebacic acid is undoubtly due to the poorer quality of the Raman spectrum. The bands are due to symmetric and asymmetric CH_2 stretching, OH stretching, and to overtones and possibly combinations. In this range of 3000 to 2700 cm^{-1} it is highly likely that the near (accidental) degeneracy of a number of bands of the same species gives rise to Fermi resonance. Fermi resonance between combination or overtone bands and fundamentals can cause an enhancement of the overtone bands and a loss of intensity of the fundamental bands, i.e., Fermi resonance allows the combination vibrations to "borrow intensity" from fundamentals. This phenomenon makes difficult the assignment of some of these bands to particular vibrations.

It has been established in the infrared spectrum of adipic acid that the O-H stretching band, lowered by hydrogen bonding, is slightly higher in frequency than the CH_2 stretching bands.[85] Generally the methylene bands are found as structure on the broad, strong O-H stretching absorption band. In the Raman spectrum methylene stretching bands have been found to be intense, but hydroxyl stretching bands appear to be faint. No one band in the Raman spectrum of any of these acids could be assigned to O-H stretching. The bands in this region in the Raman spectra of n-C_{36} (See Table II-2), tetradecanedioic, and sebacic acids are very similar in frequency and intensity. This region has been interpreted tenatively for each acid in terms of the CH_2 stretching vibrations and overtones. The most intense of the higher frequencies are assigned as asymmetric methylene stretching, while the next in intensity and lower in frequency have been assigned to symmetrical methylene stretching.

Methylene Rocking-Twisting Vibrations

As previously mentioned, normal coordinate analyses by Snyder and Schachtschneider have shown that the rocking and twisting modes of the methylene groups are mixed. Those bands which are predominately due to rocking are found between 1050 to 700 cm^{-1} while those bands predominately due to twisting are found between 1300 to 1175 cm^{-1}. Heavy carboxyl absorptions in the 1000-950 cm^{-1} region and above 1250 cm^{-1} make it difficult to observe the weak infrared CH_2 twisting bands. However, the infrared rocking bands may be observed easily between 950 cm^{-1} and 700 cm^{-1} in all the acids, the number of bands increasing with the chain length. In none of the acids studied is the complete series of methylene rocking

bands, i.e., n/2 double bands, clearly observed. It has been speculated that the two CH_2 groups nearest the carboxyl end groups do not participate effectively in the rocking motion.[60] Susi has identified one a_u, b_u rocking doublet in the infrared spectrum of adipic acid at 732, 736 cm^{-1}. He also reports, but does not assign, a very weak band at 787 cm^{-1} which is apparently the other a_u, b_u rocking doublet, since a rocking band is found at 795 cm^{-1} for suberic acid. This would account for the complete series of two doublets, without making the peculiar assumption that the α-CH_2 groups do not participate in the rocking. It is more likely that the carboxyl absorption from 1000 to 950 cm^{-1} masks the unobserved rocking bands. For suberic acid, two doublets, out of three possible, have been observed with certainty. Possibly the third rocking band is located at 972 cm^{-1}, where it is heavily masked. In sebacic acid all of the infrared-active rocking fundamentals have been identified. However, for tetradecanedioic only half of the six infrared rocking doublets have been observed.

In the longer-chain n-paraffins and monobasic acids the rocking bands have been found to be regularly spaced. However, in these shorter chains, the interval between rocking bands decreases toward lower wavenumber. The splitting of the a_u, b_u doublets in the rocking series can probably be explained by interaction between vibrations in adjacent chains.

Raman bands which might be attributed to rocking have not been noted in this laboratory for any of these acids, nor for other samples with methylene chains. Ananthanarayanan[17] has reported bands in the 700 cm^{-1} region for both adipic and sebacic acid which could be attributed to methylene rocking. These bands are very weak and are on the threshold of

detectability in his densitometer tracings.

Methylene Deformation Vibrations

While one might expect a series of bands corresponding to methylene bending vibrations, no such series but only what appears to be two bands have been observed. All n-paraffins longer than n-C_4H_{10} show strong absorption near 1470 cm^{-1} which has been assigned to methylene deformation. A strong Raman band appears in the spectrum of polyethylene at 1440 cm^{-1} which is apparently the low frequency limit of the expected series.[25] This then would confine the n/2 possible doublets due to methylene deformation to lie between 1470 and 1440 cm^{-1}, making detailed assignments difficult. However, two strong bands occur in the infrared spectrum of the dibasic acids which may be assigned with certainty to methylene deformation vibrations. The a_u, b_u doublet near 1460 corresponds to the upper limit of the methylene deformations. The band near 1400 cm^{-1}, an unresolved a_u, b_u doublet in most of the spectra, is due to methylene bending of the methylene groups adjacent to the carboxyl group.[101] The other deformation modes are probably weak in intensity. Raman bands are found near 1400 and 1460 cm^{-1} which undoubtedly represent Raman-active methylene deformation modes. These bands increase in intensity relative to the C=O stretching band as the chain length increases.

Methylene Chain Vibrations in the 1350-950 cm^{-1} Region

In the spectral range between 1350 and 950 cm^{-1} distinct series of bands occur in the infrared spectra of the longer n-paraffins and monobasic acids. These have been assigned to methylene wagging, methylene twisting, and skeletal stretching modes. In the shorter chains these

overlapping series are more difficult to separate, and it is possible that considerable mixing takes place between the various modes. The strong carboxyl band at 1300 cm^{-1} masks methylene bands near this frequency.

Between 1000 and 1175 cm^{-1} a series of a_u, b_u doublets can be observed. These bands have been assigned as skeletal modes. The a_u component is usually stronger than the b_u component, which may be caused by an interaction with the carboxyl groups.

Medium intensity Raman bands near 1090 cm^{-1} and 1050 cm^{-1} observed in these acids have been assigned to skeletal deformation corresponding to the 1131 and 1061 cm^{-1} bands observed in the Raman spectrum of polyethylene. Weaker Raman bands in the 1000 to 1175 cm^{-1} region are believed to be primarily skeletal modes.

The upper series of the twisting-rocking modes occur in the 1175 to 1375 cm^{-1} region. Bands occurring between 1200 and 1300 cm^{-1} have been assigned to this series. The strong band occurring near 1290 cm^{-1} in the infrared spectra is primarily caused by C-O stretching and OH bending with some mixture of twisting-rocking of the methylene groups. The Raman band near 1300 cm^{-1} must be primarily due to CH_2 twisting, since its relative intensity increases with chain length as compared to the C=O stretching band. This corresponds to the 1295 cm^{-1} twisting fundamental observed in polyethylene. Weak infrared and Raman bands occurring between 1300 and 1400 cm^{-1} have been attributed to methylene wagging.

Odd Acids

The monoclinic unit cell structure of the α- and β-forms of the odd acids is discussed in Chapter IV. There are four molecules per unit cell for both forms. The two shorter axes are orthogonal and are designated

by the letters a and b. The methylene chains are approximately parallel to the c-axis, which is also perpendicular to the b-axis and makes an angle β with the a-axis. The angle β is generally larger in the β-form than the α-form.

The space group C_{2h}^5 has been described previously. The unit cell of space group C_{2h}^6 possesses eight inversion centers, two glide planes, and four two-fold axes.[112] The four odd-acid molecules in the unit cell possess the symmetry C_2.

If an analysis is made on the basis of the molecular symmetry C_2 vibrations of species a and b are obtained. The presence of four molecules in the unit cell causes the number of vibrations to quadruple, each a vibration giving rise to 2 a_g and 2 a_u vibrations, and similarly each b vibration giving rise to 2 b_g and 2 b_u vibrations. The difference between the a_u and a_g fundamentals and between b_u and b_g fundamentals is a matter of phase differences between the vibrations of the molecules in the unit cell. It is doubtful that all the fundamentals associated with a particular group vibration can be resolved in the observed spectra. Vibrations of species a_u and b_u are only infrared-active, and vibrations of species a_g and b_g are only Raman-active. However, it is expected that there will be a number of near coincidences in frequency between infrared and Raman bands. The Raman-active fundamentals that are symmetric or antisymmetric with respect to C_2 belongs to species a_g or b_g, respectively. The infrared fundamentals symmetric or antisymmetric to C_2 belong to species a_u or b_u, respectively.

The odd acids are not planar, the carboxyl groups tilting $\sim 30^\circ$ out of the plane of the carbon skeleton. Hence it is not generally feasible

to speak of in- and out-of-plane motions. It has been shown for the α-form that the skeletal planes of the four molecules are approximately parallel to the bc-plane of the crystal. Van der Helm believes the skeletal planes in the β-form could also be parallel to the bc-plane. The spectrum of β-azelaic acid supports this belief. Hence planar motions of the methylene chain should be polarized parallel to the bc-plane, while out-of-plane methylene chain motions should be polarized perpendicular to the b-and c-axes. For the even acids the a_u vibrations are polarized strictly along the b-axis, but for the odd acids neither the a_u or b_u vibrations are polarized strictly along one axis.

As with the even acids, the vibrations due to the carboxyl groups are fixed in number and more or less in frequency. The polarization of the vibrations due to the eight carboxyl groups are difficult to ascertain, and the bands will generally have components along all crystallographic axes. The vibrations, their species and polarizations, are summarized in Table VI-2.

The polarized infrared spectra of azelaic acid, $HOOC(CH_2)_7COOH$, (Fig. V-9) shows absorption parallel to the a-axis and b-axis, respectively. The spectra of pimelic acid, $HOOC(CH_2)_5COOH$, (Fig. V-7,8) are assumed to show absorption approximately parallel to the a-axis and perpendicular to the a-axis. The spectra of glutaric acid, $HOOC(CH_2)_3COOH$, (Fig. V-5) is assumed to show absorption approximately parallel and perpendicular to the a-axis. The only densitometer tracing of the Raman spectrum of an odd acid given here is that of pimelic shown in Fig. V-3. The vibrational bands and their interpretations are given in Tables V-2,4,6.

TABLE VI-2

VIBRATIONAL SPECIES OF ODD DICARBOXYLIC ACIDS
$HOOC(CH_2)_nCOOH$, $n = 1,3,5,\cdots$

Vibrations	Unit Cell Species	Infrared Polarization[a] a_u	b_u
Methylene Group	$6n(a_g + a_u + b_g + b_u)$		
sym. CH_2 stretching	$(n+1)(a_g + a_u) + (n-1)(b_g + b_u)$	b	$(\perp b,c)^*$
CH_2 deformation	same	b	$(\perp b,c)^*$
CH_2 twisting	same	$(\perp b,c)^*$	$\perp b, \perp c$
asym. CH_2 stretching	$(n-1)(a_g + a_u) + (n+1)(b_g + b_u)$	$(\perp b, \perp c)^*$	$\perp b, \perp c$
CH_2 wagging	same	$(\perp b, \perp c)^*$	$\perp b, \perp c$
CH_2 rocking	same	$(\perp b, \perp c)^*$	$\perp b, \perp c$
Skeletal[b]	$(3n+1)(a_g + a_u) + (3n-1)(b_g + b_u)$		
in-plane	$(2n+2)(a_g + a_u) + 2n(b_g + b_u)$	b	--
out-of-plane	$(n-1)(a_g + a_u) + (n-1)(b_g + b_u)$	--	$\perp b, \perp c$
COOH Group	$18(a_g + a_u + b_g + b_u)$		
<u>in-plane</u>			
C=O stretching	$2(a_g + a_u + b_g + b_u)$		
C-O stretching	same		
O-H stretching	same		
O-H bending	same		
O-C=O angle bending	same		
<u>out-of-plane</u>			
C=O bending	same		
C-O bending	same		

TABLE VI-2 (Continued)

Vibrations	Unit Cell Species	Infrared Polarization[a] a_u	b_u
O-H bending	same		
O-C=O torsion	same		
TOTAL	$(9n + 19)(a_g + a_u) + (9n + 17)(b_g + b_u)$		

[a]The symbols b and ⊥ b,c indicate that the band should appear with the electric field in the incident radiation polarization along the b-axis and perpendicular to the b-axis (approximately parallel to the c-axis), respectively. The symbol ⊥b, ⊥c indicates that the band should appear with the electric field in the incident radiation polarized perpendicular to both the b- and c-axes. The symbol ()* indicates that the band is essentially forbidden and should appear only weakly, if at all.

[b]In enumerating the skeletal vibrations three translations and three rotations have been subtracted. This ignores certain low frequency vibrations.

The most useful data are gained from the Raman spectra of ordinary and partly deuterated pimelic acid, $HOOC(CH_2)_5COOH$ and $DOOC(CH_2)_5COOD$, and the infrared spectra of the β-azelaic acids, $HOOC(CH_2)_7COOH$ and $DOOC(CH_2)_7COOD$. The interpretation of the odd acid spectra will be based mainly on these spectra. The infrared spectra of glutaric and the α- and β-forms of pimelic acid will be discussed separately.

Carboxyl Group Bands

The carboxyl bands also dominate the infrared spectra of the odd acids. While the even acids had one a_u and one b_u fundamental for each COOH mode of vibration, the odd acids possess two a_u and two b_u for each mode. Because of the hydrogen bond coupling between COOH groups, and the apparent coupling between skeletal and COOH vibrations, it is possible for certain COOH vibrations that all four of these infrared active bands may have been observed in the spectrum of azelaic acid. All of the COOH bands can be expected to have both a- and b-components in the spectra of azelaic acid.

The infrared spectra of the odd acids the C=O stretching frequency is observed at approximately 1695 cm^{-1}. For the COOD form of azelaic acid this band shifted slightly to approximately 1685 cm^{-1}. The corresponding Raman-active band is found at approximately 1645 cm^{-1}, and there was no noticeable shift of the band in the COOD form of pimelic acid.

A broad shoulder was found to occur near 1800 cm^{-1} in the a-component of this infrared band for these acids, but not in the infrared spectrum of the COOD form of azelaic acid. This supports the assignment of this band as a combination of Raman-active and infrared-active fundamentals involving an OH motion.

The bands observed near 1440 cm^{-1} in the infrared spectra have been assigned to C-O stretching mixed with OH in-plane bending and coupled with terminal skeletal stretching. It would be expected that this band would show a-and b-components, as it does in the COOH form of azelaic acid. However, the a-component is almost absent in the DOOH form of azelaic acid. This is probably due to the mixed nature of the band. The corresponding bands in the Raman spectra are probably caused by a mixture of the same motions. However, since the Raman band increases relative intensity with chain length, it is probable that methylene deformation bands may also overlap these bands in this region.

The band near 1300 cm^{-1} in the infrared spectra has been assigned to in-plane O-H bending mixed with C-O stretching. It is possible also that the wagging mode of the adjacent methylene groups overlaps effectively with C-O stretching motion, since the Raman band occurring near 1300 cm^{-1} increases in relative intensity with the chain length. In the infrared spectrum of the DOOC form of azelaic acid the in-plane O-H bending band is shifted to 1053 cm^{-1}, and the band near 1300 cm^{-1}, due principally to C-O stretching, is weakened. Neither of the Raman bands found at 1450 cm^{-1} and 1270 cm^{-1} for ordinary pimelic acid were shifted in the Raman spectrum of DOOC-pimelic acid. The O-D motions appear not to mix effectively with the Raman-active C-O stretching motion.

Two weak bands with a and b polarizations, respectively, are found at 1356 and 1335 cm^{-1} in the infrared spectrum of COOH-azelaic acid. These may also represent C-O stretching. However, it is also possible that these bands arise from methylene wagging. Very intense bands occur at 1366 (a) and 1362 (b) cm^{-1}, and 1340 (a,b) cm^{-1}, in the spectrum of

DOOC-azelaic acid. If these bands were due simply to methylene wagging no apparent reason can be given for such high intensity.

Information on the infrared-active out-of-plane O-H vibrations is obscured due to the great intensity of these unresolved bands. In the COOD form of azelaic acid these bands are shifted to near 700 cm^{-1}, but are still very intense. In the Raman spectrum of COOH-azelaic acid a medium-weak band is found at 902 cm^{-1} which may correspond to out-of-plane O-H vibration, but is more likely caused by terminal skeletal stretching. In the Raman spectrum of COOH-pimelic acid a weak, sharp band is found at 939 cm^{-1}, and a strong band is observed at 899 cm^{-1}. In the Raman spectrum of COOD-pimelic acid a single medium-strong band was observed at 870 cm^{-1}. This is undoubtedly the 899 cm^{-1} band shifted. That a band corresponding to the 939 cm^{-1} band was not observed can be accounted for by the poor quality of the COOD Raman spectrum. Due to the small shift of the 899 cm^{-1} band it is not likely that it arises from a vibration directly involving the hydroxyl group. It is probably a stretching mode involving the terminal skeletal C-C bond coupled to the hydroxyl group. The weak band at 939 cm^{-1} is probably an out-of-plane O-H bending mode.

In the even acids an a_u, b_u doublet was observed near 690 cm^{-1} which is undoubtedly due to O=C-OH angle deformation. In the infrared spectrum of azelaic acid two a_u, b_u doublets have been observed which may be assigned to this motion. In the spectrum of HOOC-azelaic acid bands are observed at 681 (b), 676 (a) cm^{-1} and 612 (b), 609 (a) cm^{-1}. The splitting of these two doublets is the same, the b-component being the higher in intensity and frequency. The lower frequency doublet is weaker in intensity. In the spectrum of DOOC-azelaic acid bands are observed

at 650 (a), 635 (b) cm^{-1} and 585 (a), 572 (b) cm^{-1}, respectively. In this case, the a-component is higher in intensity and frequency. There is little doubt that these are corresponding bands, but their splitting is reversed when OH is replaced by OD. The magnitude of the splitting remains essentially the same. It is striking that the 681-676 cm^{-1} doublet is shifted 36 cm^{-1}, and the 612-609 cm^{-1} doublet 32 cm^{-1} by the deuteration of the hydroxyl group making the spacing between these two doublets almost the same. It would appear that these two doublets, though split by $\sim$ 65 cm^{-1}, are both due to O=C-O angle deformation and represent the 2 a_u, 2 b_u fundamentals. In the infrared spectrum of pimelic acid two similar pairs of bands have been observed. For glutaric acid the situation is not clear.

In the Raman spectrum of pimelic acid a weak, diffuse band located at 673 cm^{-1} shifts to 638 cm^{-1} when the hydroxyl groups are deuterated. A weak, diffuse band located at 585 cm^{-1} in ordinary pimelic acid was not observed in the spectrum of the deuterated acid. This may simply be due to the fluorescent background of the DOOC-pimelic acid spectrum. A weak, diffuse band at 672 cm^{-1} and a very weak band at 592 cm^{-1} were observed in the Raman spectrum of glutaric acid. These bands have been assigned to the O=C-OH angle deformation.

While the splitting between these doublets is large, this may be accounted for by interaction between COOH groups through the rather strong hydrogen bonding. Van der Waals interaction between methylene groups in long methylene-chain compounds can cause splittings up to 10 cm^{-1}. It is therefore reasonable to expect that the interaction due to hydrogen bonding may cause much larger splittings of vibrations of the COOH groups.

In the infrared spectrum of azelaic acid two doublets, opposite in polarization, occur near 532 cm^{-1} and 506 cm^{-1}. These bands shift only slightly upon deuterating the hydroxyl groups, but the polarization and shape of the bands change considerably. Tentatively, these bands have been assigned to out-of-plane C-O bending. If this assignment is correct it is apparent that the hydrogen atom has a larger effect upon in-plane bending of the C-O group than on out-of-plane bending.

Two doublets in the infrared spectrum of azelaic acid near 443 and 405 cm^{-1} suffer very slight changes upon deuteration of the OH groups. In the DOOC-spectrum the splitting of each doublet is more pronounced, but the bands do not shift appreciably in frequency. These bands have been assigned to a mixture of out-of-plane C=O bending and O=C-O torsion. The skeletal deformation modes could well have an affect upon these motions, particularly deformations involving the C-C bonds adjacent to the COOH groups.

For pimelic acid a weak Raman band was observed at 517 cm^{-1}. This band was found at 515 cm^{-1} in the Raman spectrum of pimelic acid with deuterated hydroxyl groups. For glutaric acid a weak Raman band at 438 cm^{-1} was noted. These bands are probably due also to COOH motions mixed with skeletal deformations.

The bands observed in the 650-400 cm^{-1} infrared region for the odd acids are similar to those found for the even acids. Since it has been fairly well established that these bands do not occur, or at most occur extremely weakly, in a methylene chain compound which does not possess COOH-end groups, these bands most likely are due to the COOH groups. However, the low frequency motions of these end groups probably

are coupled to low frequency skeletal deformation modes. Moreover, because of the strong hydrogen bonding it may not be feasible to characterize these bands in a simple manner. Unfortunately the polarization data obtained for these bands are not useful for making definite assignments since the orientations of COOH groups in β-azelaic acid are unknown.

Methylene and Hydroxyl Stretching Vibrations

Similar to the Raman spectra of the even acids, the Raman spectra of the odd acids exhibit numerous strong bands in the 2800 to 3000 cm^{-1} region. The pattern of these bands is similar in frequency, but different in relative intensity from those observed for the even acids. The intensity pattern of methylene stretching bands is apparently very sensitive to the packing of the molecules and the number of molecules per unit cell. The Raman spectrum of $DOOC(CH_2)_5COOD$ in this region was the same as the Raman spectrum of $HOOC(CH_2)_5COOH$. This supports the assumption that the hydroxyl stretching vibration has little affect on the pattern of these bands. Like the even-acid bands, the observed odd-acid bands in this region have been assigned to symmetrical and asymmetrical methylene stretching and combination bands.

Methylene Rocking-Twisting Vibrations

The rocking modes should possess strong b_u fundamentals polarized perpendicular to the skeletal plane. For azelaic acid, the prominent lowest frequency rocking band is observed to be polarized with a strong component in the direction of the a-axis, and with only an extremely weak component parallel to the b-axis. This indicates that the skeletal planes of the four molecules in the unit cell are approximately parallel to the

crystallographic bc-plane. The a_u fundamentals should at most possess a very small component parallel to the b-axis.

In the infrared spectrum of β-azelaic acid three a_u, b_u rocking doublets have been observed, a fourth a_u, b_u rocking doublet being obscured by the intense OH out-of-plane bending vibration. In the spectrum of β- azelaic acid with deuterated hydroxyl groups four such doublets are noted. The b component of the rocking doublet at 821 cm^{-1} is obscured by an overlapping skeletal vibration band. Eight (a_u + b_u) methylene rocking bands should be observable. Since only four doublets are noted, each of the observed a_u bands is in all probability composed of two unresolved a_u fundamentals. The same assumption applies to the b_u rocking bands. While a weak Raman band has been observed for pimelic acid at 768 cm^{-1}, it is doubtful that this is a rocking band, since it was not observed in any other Raman spectrum of these acids.

Methylene Deformation Vibrations

As in the case of even acids, the (n + 1) (a_u + b_u) methylene deformation bands of the odd acids should be found between 1470 and 1440 cm^{-1}. The bands should be polarized mainly parallel to the b axis. The strong band at 1458 cm^{-1} polarized parallel to the b axis observed in the spectrum of azelaic acid is undoubtedly due to methylene deformation. This band is not affected by deuteration of the hydroxyl group. The strong band observed at 1406 cm^{-1} is usually found in any compound with a CH_2 group adjacent to the highly polar COOH end group. This band has both a- and b-components, and hence may not be strictly a methylene deformation mode. However, the CH_2 group adjacent to the end group is twisted

out of the skeletal plane as shown in Fig. IV-3. This may explain the appearance of both a-and b-components. It is possible that the methylene deformation and wagging modes are coupled in case of the α-CH_2 groups. This would explain the large a-component. This band does not change at all upon deuteration of the hydroxyl group. The Raman band observed near these frequencies in all the acids studied was found to increase in relative intensity with increasing chain length.

Methylene Chain Vibrations in the 1400 - 800 cm^{-1} Region

In the region between 1400 and 800 cm^{-1} series of bands occur which can be assigned to methylene wagging, methylene twisting, and skeletal stretching modes. In the spectrum of ordinary β-azelaic acid the strong carboxyl bands near 1300 cm^{-1} and 925 cm^{-1} obscure information on the methylene chain vibrations. In the deuterated-hydroxyl form of azelaic acid these bands are shifted to near 1050 and 700 cm^{-1}.

Bands occurring near 1360 and 1340 cm^{-1} in the spectra of both the ordinary and the DOOC-azelaic acid have been assigned to a mixture of methylene wagging and carboxyl motions. These bands have already been discussed. Bands occurring between 1300 and 1200 cm^{-1} have been interpreted as principally methylene twisting modes. While these should possess only a-components, it is possible that the wagging modes are coupled with the twisting modes and alter the polarization of these bands.

The strong bands centered around 1100 cm^{-1} may be due to skeletal modes coupled with COOH motions, since their intensities are decreased when the hydroxyl groups are deuterated. Skeletal stretching modes, polarized parallel to the b-axis, are observed in both spectra in the

region between 1000 and 800 cm^{-1}. However, the spectrum of azelaic acid with deuterated hydroxyl groups shows this series better.

Pimelic Acid

It is likely that the α- and β-forms of the odd acids are structurally similar, the primary difference being in the packing of the COOH groups. The α-form of glutaric and pimelic acids has been shown by x-ray diffraction to be built on the same principle. It can be assumed that α-azelaic acid is very similar to both of these acids. Unfortunately, no x-ray diffration work on the structure of the β-form of the odd acids has been reported. However, it is probable that this form is also similar for these acids.

Both α-glutaric and α-pimelic acids have four molecules per unit cell arranged so that their skeletal planes are parallel to the crystallographic bc plane. Spectroscopic evidence indicates strongly that the β-form of azelaic acid also has the skeletal planes of the molecules parallel to the bc-plane.

The crystals of pimelic acid used in this study were of somewhat inferior quality. The crystals were irregular flakes with a heavy mosaic. Neither the crystal form nor the habit could be ascertained with the use of a polarizing microscope. The quality of the spectra obtained was generally poor. One such spectrum is shown in Fig. V-7. The incident polarized electric vector was parallel to the crystal flake in the directions which yielded the maximum absorption difference of the lowest frequency rocking band.

This crystal was heated to 80°C and held at this temperature for 24 hours. The crystal mosaic was considerably cleared by this treatment.

The spectra were obtained with the same orientations of the electric vector relative to the crystal. The spectrum in the region from 1100 to 400 cm^{-1} was different from that observed previously, as is shown in Fig. V-8. The quality of the region above 1100 cm^{-1} was very poor. It is evident that a transition to the high-temperature β-form, occurred. This procedure was used with two other crystals with the same result. The spectra obtained closely match the spectra of β-azelaic acid in the region from 1000 to 700 cm^{-1}.

The rocking bands of the α-form of pimelic acid should be polarized perpendicular to both the b-and c-axes with a resultant in the direction of the a-axis. The same conclusion holds for the β-form of pimelic acid if it is assumed that the skeletal planes are approximately parallel to the bc-plane as they are in the β-form of azelaic acid. The spectra of the β-form of pimelic acid shows the low frequency rocking band to possess a maximum for one orientation with only a very weak component for the other orientation. In the case of the α-form the situation is not as clear. The maximum intensity of the rocking band of the α-form occurs in the dashed curve, while the opposite is true in the β-form. The assumed polarizations shown for the incident electric vector in both Fig. V-7, 8 are not quite certain, since the crystallographic axes may have changed slightly in the crystal flake when the transition from the α- to the β-form occurred.

The bands of these two forms have been listed and interpreted in Table V-4. Since the orientation of these crystals is somewhat uncertain and since little is known about the structure of the β-form of pimelic acid, a detailed discussion of these bands will not be given. The apparent

polarization of the bands has been considered, and a comparison has been made between these spectra and that of azelaic acid in making the interpretations. The interpretation of the pimelic acid spectra appears fairly consistent with that of the spectra of the other acids. The Raman spectra of both $HOOC(CH)_5COOH$ and $DOOC(CH_2)_5COOD$ have been discussed along with the interpretation of the azelaic acid spectrum.

Glutaric Acid

Only a single crystal of glutaric acid was grown which could be used to obtain the infrared spectrum shown in Fig. V-5. The crystal was a thin, heavily striated flake whose form and habit was uncertain. From the spectrum obtained, and the similarity of the striations on this crystal and on the adipic acid crystal it has been assumed that the crystal flake was approximately parallel to an ac-plane. Moreover, it was assumed to be of the α-form, since this is the form stable at room temperature. In an effort to cause an α- to β-form transition this crystal was lost. No detailed discussion will be made of the assignment of the vibrations. The observed infrared and Raman bands are listed and interpreted in Table V-2.

Low Frequency Raman Bands

It is well known that a band should occur in the Raman spectrum of a molecule containing an extended methylene chain which corresponds to the longitudinal frequency characteristic of a rod whose length equals the chain length, and whose "stiffness" is determined by the chain bonds. As the chain length increases, this frequency decreases. Shimanouchi and Mizushima[114] have observed such a low frequency band for the solid

normal paraffins which varies from 425 cm^{-1} for $CH_3(CH_2)_2CH_3$ to 150 cm^{-1} for $CH_3(CH_2)_{14}CH_3$.

Ananthanarayanan[17] has recently reported some fairly strong Raman shifts, 325 cm^{-1} and lower, for sebacic and adipic acid. He interprets these bands as hydrogen bond vibrations. However, he reports no such bands for malonic or succinic acids, where the density of COOH dimeric rings is much higher. Such bands would be expected to be more intense for these samples.

The frequency of a hydrogen bond vibration will depend upon the strength of the bond, which may be expressed in terms of the length of the hydrogen bridge, $R_o = 2.68 \pm 0.05A$, and the masses of the hydrogen bonded constituents. This is, of course, a much simplified view. For adipic and sebacic acids R_o is essentially the same. Hence, the fundamental hydrogen bond frequency would be expected to be lower for sebacic acid, $HOOC(CH_2)_8COOH$, than for adipic acid, $HOOC(CH_2)_4COOH$. However, Ananthanarayanan assigns a band at 304 cm^{-1} for adipic acid and 329 cm^{-1} for sebacic acid as the fundamental hydrogen bond frequencies. While this interpretation is questionable, the higher frequency for sebacic acid may be caused by a change in the hydrogen bond frequencies. While this interpretation is questionable, the higher frequency for sebacic acid may be caused by a change in the hydrogen bond force constant due to a slight change ($\pm$ 0.05A) in R_o.

More recently, normal corrdinate calculations have made certain that the bands observed in the infrared at 188 cm^{-1} for the acetic acid dimer, $(CH_3COOH)_2$, and 237 cm^{-1} for the formic acid dimer, $(HCOOH)_2$, must be assigned to hydrogen bond stretching.[113] However, while these

compounds possess doubly-hydrogen bonded carboxyl groups, they do not have methylene chains.

In this study bands were found at 411 cm^{-1} for malonic acid, at 384 cm^{-1} for succinic acid, at 344 and 314 cm^{-1} for glutaric acid, at 298 cm^{-1} for adipic acid, and at 324 and 267 cm^{-1} for pimelic acid. For the partially deuterated sample of pimelic acid, $DOOC(CH_2)_5COOD$, the bands did not shift appreciably in frequency, being found at 323 and 265 cm^{-1}. That bands of low frequency were not observed for the other acids can be attributed to the poorer quality of the spectra. The assignment of these low frequency bands poses a difficult problem.

These bands form a progression of decreasing frequency and relative intensity with increasing chain length. Whether they are due to skeletal modes or to hydrogen bond vibrations, such a progression and decrease in relative intensity might be expected. Moreover, the fact that the two low frequency bands observed for pimelic acid did not shift upon partial deuteration does not yield useful information, since both these forms of motions should be relatively insensitive to such deuteration. It is difficult to determine whether or not Ananthanarayanan's agreement between the theoretically calculated and observed hydrogen bond frequencies is fortuitous. There is probably considerable mixing between the hydrogen bond vibrations and the low frequency skeletal modes. Until a normal coordinate analysis is made on such a system, it will be difficult to ascertain what interaction occurs between the skeletal and hydrogen bond motions. The low-frequency Raman bands observed in this study have been assigned simply to a mixture of these motions.

Concluding Remarks

The present study has provided both Raman and polarized infrared data on a series of similar compounds containing methylene chains. Few investigators ever report both Raman and infrared data, and even fewer report data on a homologous series. Unfortunately, even in this study the data were not consistently excellent, but the data obtained have allowed certain conclusions to be drawn. Assignment of many of the fundamentals of the dibasic acids has been accomplished.

The Raman data, sensitive to the concentration of the various atomic groups composing the molecule, have indicated that bands of similar frequency in the infrared and Raman spectra of the dibasic acids need not be caused entirely by the same vibrations. In particular, the band occurring in the infrared spectra of the dibasic acids near 1300 cm^{-1} has been assigned to a mixture of the C-O stretching and O-H bending vibrations. The band found near this frequency in the Raman spectra cannot be due strictly to COOH vibrations since its intensity relative to the C=O band increases with chain length. Hence this band must be attributed to a mixture of C-O stretching, O-H bending, and overlapping of bands caused by methylene wagging motions. As the chain length increases the methylene wagging bands evidently cause the increase in relative intensity. Similar conclusions were drawn for the band occurring near 1430 cm^{-1} in the infrared and Raman spectra.

The development of the methylene rocking band series with increasing chain length has been observed. The other band series characteristic of the methylene groups (deformation, wagging, twisting) have not been observed clearly, primarily because of overlapping, intense

carboxyl bands.

In all of the infrared spectra of these acids several prominant bands between 700 and 400 cm^{-1} have been assigned to out-of-plane motions associated with the carboxyl group. While these frequencies may appear slightly high for such motions, the hydrogen bonding may contribute effectively in raising the frequency. That these bands are due at least in part to the COOH end groups has been demonstrated by their apparent absence in the spectrum of a long methylene chain alcohol. In all probability these COOH motions may be vibrationally coupled to the low frequency skeletal modes. Further investigation of these bands is warrented. Since the COOH groups are more nearly coplanar with the carbon skeleton in the even acids, a polarized infrared study of these bands using docosanedioc acid, $HOOC(CH_2)_{20}COOH$, docosanoic acid, $CH_3(CH_2)_{20}COOH$, and docasanol alcohol, $CH_3(CH_2)_{20}CH_2OH$, should provide conclusive information. It should be possible to grow crystals of comparable thickness of these three compounds so that the relative intensity of the bands can be compared.

Previously, no Raman or polarized infrared data have been available on any of the odd dibasic acids. The infrared data presented here on the β-form of azelaic acid have indicated that the skeletal planes of the molecules are parallel to the crystallographic bc-plane, as they are known to be for the α-form. Moreover, the large splitting of the bands assigned to the deformation of O=C-O has demonstrated the affect of the hydrogen bonding on the carboxyl motions.

The infrared spectra of pimelic acid, although of poor quality, have shown the large changes which occur when a transition is made from

the α- to β-form of an odd acid crystal. Since the crystal orientation was uncertain, further investigation of the α- to β-form transition and its affect on the infrared and Raman spectra should be worthwhile. To date no corresponding difference between the Raman spectra of different polymorphs of the same long methylene chain compound has been reported. The Raman spectra of the $HOOC(CH_2)_5COOH$ and $DOOC(CH_2)COOD$ samples have demonstrated that the hydroxyl group probably does not couple well with the other Raman-active vibrations, since only two of the observed bands, neither of which were OD bands, were appreciably shifted. No OD bands were observed since the DOOC-pimelic acid spectrum had an appreciable background, and the vibrations directly attributable to the OH group are apparently only weakly Raman-active.

The low frequency Raman shifts observed here and also reported by Ananthanarayanan merit further study. These frequencies lie well within the range of modern far infrared spectrometers and a study of these acids between 400 and 50 cm^{-1} in the infrared could be helpful in the assignment of these bands.

APPENDIX I

TABLE A I-1

LINES OBSERVED IN THE FOCAL-POINT

Hg-LAMP BETWEEN 4358 AND 5143 A

Wavelength[a] A	Intensity[b]	Wavenumber cm^{-1}	Shift from 4358 A cm^{-1}
4358.4	vvvs	22938.1	0.0
4385.8	w	22794.6	143.5
4391.1	w,d	22766.7	171.4
4398.6 II[c]	m	22728.3	209.8
4425.3 II	w	22591.1	347.0
4463.8	w	22396.1	542.0
4492.9 II	w	22251.2	686.9
4660.2 II	m	21452.2	1485.9
4686.4	w,d	21332.4	1605.7
4702.4 II	vw,d	21259.8	1678.3
4722.7	w,d	21168.4	1769.7
4747.5	w,d	21057.7	1880.4
4782.2	w,d	20905.0	2033.1
4797.3	vw,d	20839.2	2098.9
4821.5	w	20734.5	2203.6
4827.1	m	20710.6	2227.5
4855.0 II	m	20688.6	2346.5

TABLE A I-1 (Concluded)

Wavelength A	Intensity[b]	Wavenumber cm^{-1}	Shift from 4358 A cm^{-1}
4832.2	s	20591.6	2249.5
4882.0	vs	20477.7	2460.4
4889.8	m	20449.3	2488.8
4897.3	m	20413.5	2524.6
4915.8	vs	20390.9	2601.1
4902.8	vvs	20337.0	2547.2
4961.1	vs	20151.0	2787.1
4970.1	vs	20114.8	2823.3
4981.4	s	20069.2	2870.9
4992.4	m	20024.6	2913.5
5023.8	s	19899.7	3038.4
5045.3	s	19815.0	3123.1
5102.7	s	19591.9	3346.2
5110.0[d]	vw	19563.9	3374.2
5120.9	s	19522.5	3415.6
5128.7	s	19492.6	3445.5
5138.7	m	19454.8	3483.3
5143.5	m	19365.4	3472.7

(a) These are measured wavelengths and match known values to $\pm$ 1 A.

(b) Intensity was visually estimated from a photographic plate.

(c) These are transitions in ionized mercury and are not observed normally in mercury arc-lamps.

(d) This line has not been reported previously.

APPENDIX II

THE RAMAN SPECTRUM OF MALONIC ACID, $HOOC(CH_2)COOH$.

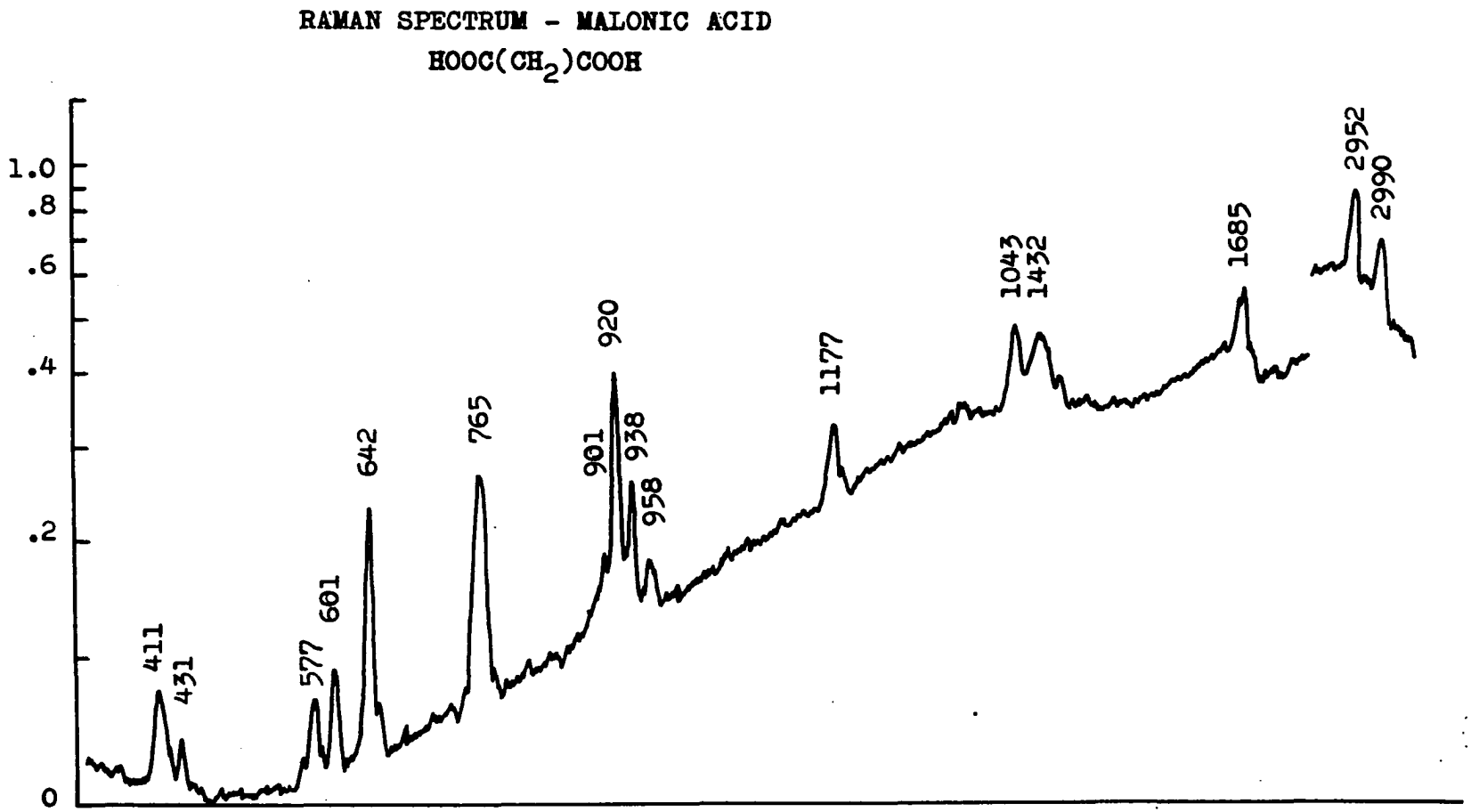

RAMAN SPECTRUM - MALONIC ACID
HOOC(CH2)COOH
1.0
.8
.6
.4
.2
0
411
431
577
601
642
765
901
920
938
958
1177
1043
1432
1685
2952
2990

Figure AII-1

APPENDIX III

THE INFRARED SPECTRA OF MYRISTIC ACID, $CH_3(CH_2)_{12}COOH$, AND MYRISTIC ALCOHOL, $CH_3(CH_2)_{12}CH_2OH$.

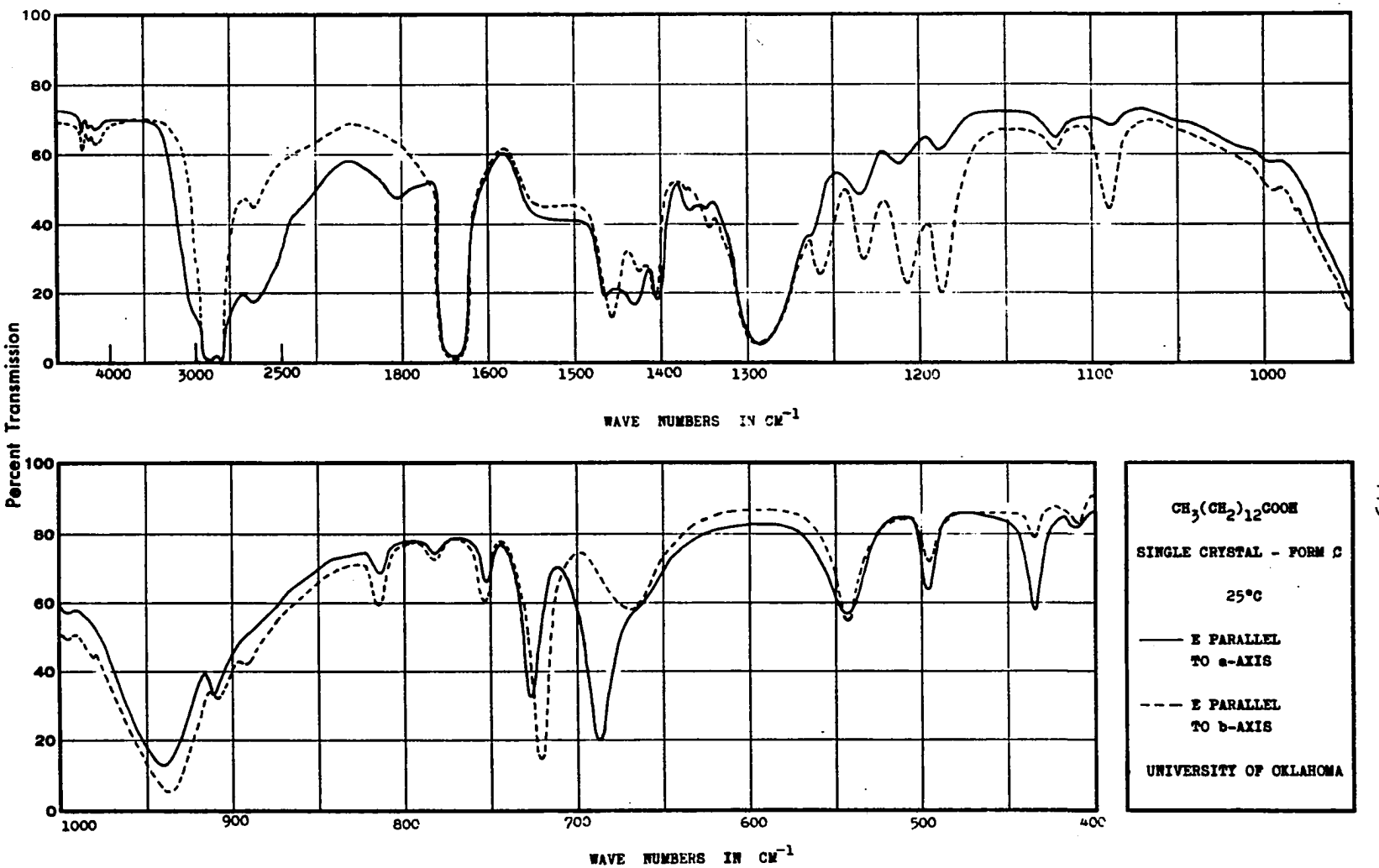


Fig. AIII-1. Infrared Spectrum of the C-Form of $CH_3(CH_2)_{12}COOH$; Radiation Incident Normal to the ab-Plane.

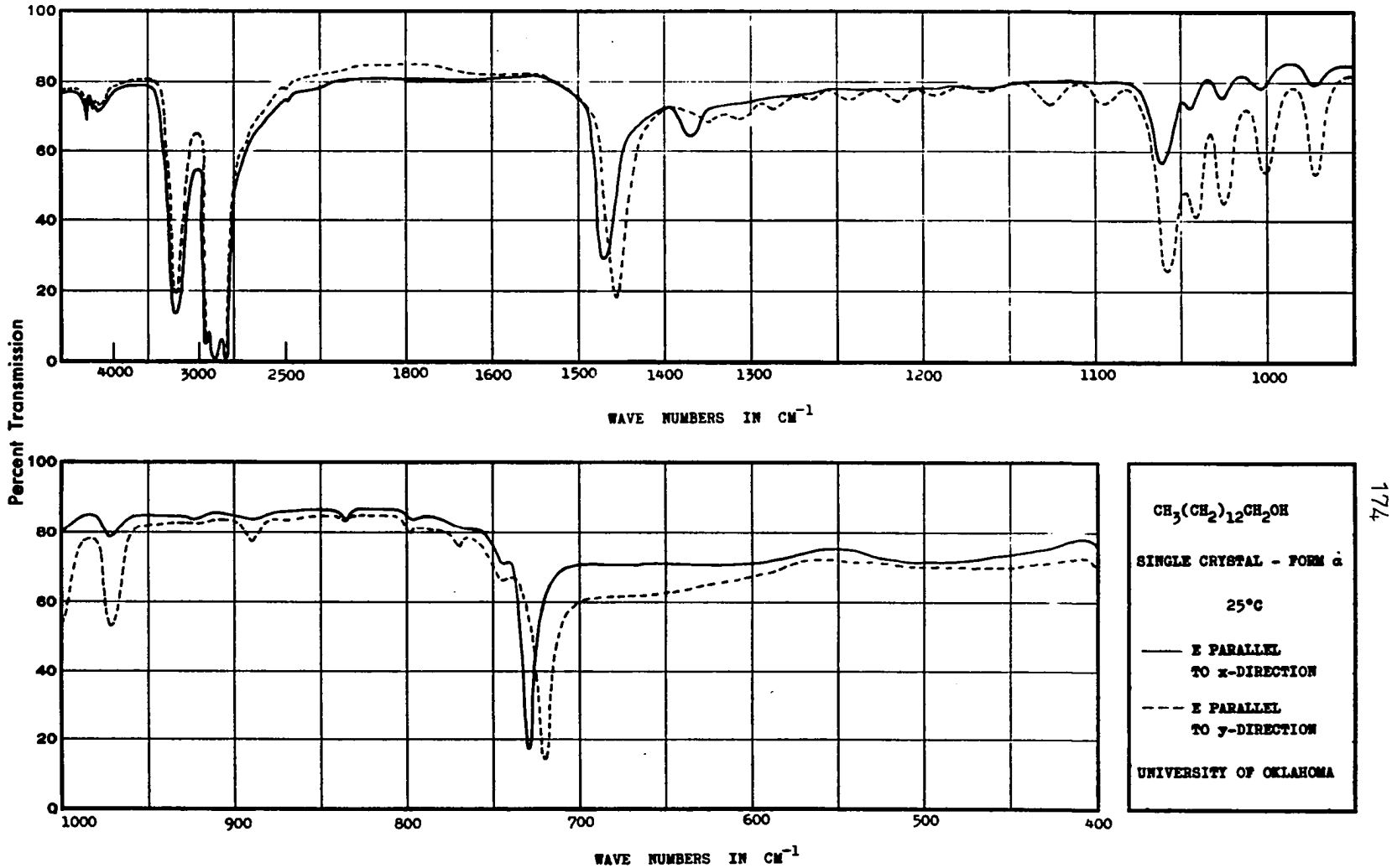


Fig. AIII-2. Infrared Spectrum of the α-Form of $CH_3(CH_2)_{12}CH_2OH$; Radiation Incident Normal to the ab-Plane.

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