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TEMPERATURE AND HYDROSTATIC PRESSURE
DEPENDENCE OF THE U-CENTER AND THE FAR
INFRARED PROPERTIES OF POLYAMINO ACIDS

by

Wayne Jefferson Shotts

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TABLE OF CONTENTS

<u>Chapter</u>		<u>Page</u>
I	INTRODUCTION.	1
	A. The U-Center Local Mode and Side Bands. . .	1
	B. Normal Modes of α -Helical Polypeptides. . .	4
	C. Plan of the Thesis	6
II	EXPERIMENTAL FAR INFRARED TECHNIQUES.	9
	A. Monochromator	10
	1. Prism Fore Optics	10
	2. Spex 1500-II Double-Pass Grating Mono- chromator	13
	3. Charcoal Vacuum Pump.	23
	B. Ge:Cu Detector and Cryostat	25
	C. Pressure Cell and Detector Insert	35
	D. Interferometers and Ge:Ga Bolometers. . . .	38
	E. InSb Electron Bolometer	43
	F. Cells for Solution Studies.	46
III	U-CENTERS IN KBr, KCl AND NaCl.	49
	A. Crystal Preparation	49
	B. Hydrostatic Pressure Measurements	53
	1. Local Mode Frequency Shift in KBr, KCl and NaCl.	53
	a. Grüneisen Constant for KBr, KCl and NaCl.	56
	b. Model Calculation of the Grüneisen Constant for KBr.	58
	c. Lattice Strain Correction	64
	2. U-Center Side Band Frequency Shift in KBr	67

<u>Chapter</u>		<u>Page</u>
III	C. Temperature Dependence of the Local Mode Linewidth.	73
	1. Adjustable Parameter Models for KBr, KCl and NaCl	73
	2. Comparison of KBr Data with Gethins' Calculation.	82
	a. Isotope Induced Frequency Shift.	83
	b. Dislocation Strain Broadening.	89
	c. Impurity Strain Broadening	92
	d. Comparison of R ₂ Zero-Phonon and U-Center 4.2°K Residual Linewidths	93
	e. Extraction of the 4.2°K Linewidth.	94
	D. The U-Center Zeeman Effect in KCl.	97
	E. Summary and Conclusions.	102
IV	FAR INFRARED ABSORPTION SPECTRA OF POLYAMINO ACIDS.	105
	A. Description of Polypeptides.	106
	B. Detection of the Far Infrared Normal Modes of the α -Helix	109
	1. Models of the Normal Vibrations.	109
	2. Measurement of the Far Infrared Absorption	113
	C. Poly- γ -benzyl-L-glutamate.	116
	D. Glycine, Alanine, Leucine and Proline.	127
	E. Poly-L-proline, Poly-L-leucine and Poly-DL-leucine.	130
	F. Alanine Oligomers and Poly-L-alanine	138
	1. Comparison of Alanine Oligomer and PLA Absorption Spectra	139
	2. Low Frequency Far Infrared Absorption of PLA.	151

<u>Chapter</u>	<u>Page</u>
IV	
G. Far Infrared Absorption of Miscellaneous Polypeptides.	.159
1. Poly(hydroxybutylglutamine-co-glycine).	.159
2. Poly-L-lysine Hydrobromide and Poly-DL-lysine Hydrobromide	.163
3. Poly-glycine.	.163
4. Myoglobin, Caesin and Egg Albumin	.163
H. Summary and Conclusions	.168
APPENDIX A. FAR INFRARED IMPURITY MODES.	.172
1. Cl^- Gap Mode in KI.	.172
2. CN^- Gap Mode in KI.	.178
3. Tl^+ Impurity Induced Absorption in RbBr and RbI	.182
APPENDIX B. FAR INFRARED ABSORPTION OF MISCELLANEOUS ORGANIC COMPOUNDS.	.185
1. Polyethylene Oxide.	.185
2. Fatty Acids	.186
3. Carbohydrates	.187
4. Nucleotides	.189
REFERENCES.	.191

LIST OF TABLES

<u>Table</u>		<u>Page</u>
2-1	Comparison of Measurements of 4.2°K U-Center Linewidths.	23
2-2	Transmission of Monochromator and Cryostat.	30
2-3	Properties of Single Crystal n-Type InSb Detector.	44
3-1	U-Center Crystal Preparation Conditions	51
3-2	Model Calculations of ω_0 and γ for U-Centers in KBr	62
3-3	U-Center Anharmonic Potential Parameters.	67
3-4	Grüneisen Constants of Features in the KBr U-Center Side Bands	73
3-5	U-Center Linewidth Determined Effective Temperature Parameters	81
3-6	4.2°K U-Center Local Mode Frequencies	87
3-7	Calculated Isotope Shifts for U-Centers in KCl.	89
4-1	Side Chains of Principal Amino Acids Studied.	107
4-2	Sources and Identification of Polypeptides.	114
A-1	Lorentzian Parameters for Cl^- Gap Mode in KI.	173
A-2	Gap Modes of Impurities Observed in KI:CN^- Spectra	180
B-1	Nucleotides Studied in the Far Infrared	190

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
2-1	Double-pass monochromator and fore optics.	11
2-2	Reference circuit.	14
2-3	Single-pass monochromator.	16
2-4	Resolution of double-pass monochromator. . .	21
2-5	Cryogenic charcoal sorption pump	24
2-6	Ge:Cu detector cryostat.	26
2-7	Ge:Cu and InSb detector bias circuits. . . .	33
2-8	Hydrostatic pressure cell and detector cryostat.	36
2-9	Interferometers and bolometers used.	41
2-10	Solution study cells	47
3-1	Additive coloration of alkali halides. . . .	50
3-2	Pressure dependent shift of KBr, KCl, and NaCl U-center local mode frequencies. . .	54
3-3	Strain induced U-center force constant change in KBr, KCl, and NaCl	66
3-4	Pressure dependence of U-center side band absorption spectrum in KBr.	70
3-5	Pressure dependent frequency shift of features in the KBr U-center side bands .	72
3-6	Temperature dependence of the KBr U-center local mode linewidth.	77
3-7	Temperature dependence of the KCl U-center local mode linewidth.	78
3-8	Temperature dependence of the NaCl U-center local mode linewidth.	79
3-9	U-center local mode absorption in KBr at 4.2°K and KCl at 54.2°K	85

<u>Figure</u>		<u>Page</u>
3-10	U-center local mode absorption in KCl and NaCl at 4.2°K.	86
3-11	Dislocation etch pits in KBr, KCl and NaCl	90
3-12	Extraction of 4.2°K linewidth from tempera- ture dependence of the KBr U-center local mode linewidth	96
4-1	Conformations of polypeptides	108
4-2	Low frequency α -helix dispersion curves . .	112
4-3	Absorption spectra of DCA and benzene . . .	117
4-4	Absorption spectra of H ₂ O, D ₂ O, benzene and chloroform	118
4-5	Transmission spectra of PLA and PBLG. . . .	119
4-6	Transmission spectrum of γ -benzyl-L- glutamate.	121
4-7	Transmission spectra of PBLG in solution and the solid state.	123
4-8	Transmission spectra of P(BLG + 3% gly) and PBLG of various lengths.	124
4-9	Transmission spectra of glycine, alanine, leucine and proline in the solid state and proline in H ₂ O	128
4-10	Transmission spectrum of poly-L-proline . .	131
4-11	Transmission spectra of poly-L-leucine and poly-DL-leucine.	134
4-12	X-ray diffraction data for polyox, PBLG, poly-L-leucine, poly-L-proline, sodium oleate and stearic acid.	135
4-13	Transmission spectra (4 to 90 cm ⁻¹) of PLA and L-alanine oligomers at 4.2°K	140
4-14	Transmission spectra (30 to 90 cm ⁻¹) of PLA and L-alanine oligomers at 300°K. . .	142
4-15	Transmission spectra (40 to 320 cm ⁻¹) of PLA and L-alanine oligomers at 4.2°K . .	143

<u>Figure</u>		<u>Page</u>
4-16	Transmission spectra (40 to 320 cm^{-1}) of PLA and L-alanine oligomers at 300°K. .	.144
4-17	X-ray diffraction data for PLA and L- alanine oligomers	.145
4-18	Transmission spectra (80 to 640 cm^{-1}) of PLA and L-alanine oligomers at 4.2°K. .	.148
4-19	Transmission spectra of PLA (DP = 30) and hexa-L-alanine.	.149
4-20	Transmission spectra of PLA (DP = 680) and tri-L-alanine	.150
4-21	Absorption coefficient of PLA (DP = 30) from 4 to 200 cm^{-1} at 4.2°K	.153
4-22	Transmission spectra of PHBG, P(HBG + 3% gly) and of PLA (DP = 680).	.155
4-23	Transmission spectra of poly-L-lysine hydro- bromide, poly-DL-lysine hydrobromide, poly-glycine and polyox	.164
4-24	Transmission spectra of ADP, poly A, starch, myoglobin and egg albumin	.165
4-25	Transmission spectrum of myoglobin	.167
A-1	Cl^- gap mode absorption in KI.	.174
A-2	CN^- gap mode absorption in KI.	.179
A-3	Tl^+ impurity induced absorption in RbBr and RbI	.183
B-1	Transmission spectra of dextrose, maltose, stearic acid and sodium oleate.	.188

ABSTRACT

The far infrared absorption properties of ionic alkali halide crystals containing U-center impurities and of covalently bonded polyamino acids are investigated. In the alkali halides, manifestations of the anharmonic potential in the impurity induced absorption are examined. For the polyamino acids, measurements in the far infrared are made to test the prediction of harmonic normal mode calculations of low frequency vibrational modes and to investigate the conformational dependence of the far infrared modes.

The temperature dependence of the U-center (H^-) local mode linewidth is measured in KBr, KCl and NaCl crystals between 4.2°K and 50°K. For KBr the residual 4.2°K strain broadened linewidth is extracted from the data, and comparison is made with previous theoretical calculations of the temperature dependence of the linewidth resulting from anharmonic coupling to the lattice phonons.

A different measure of the anharmonicity results from application of hydrostatic pressure to the crystals. Hydrostatic pressures of up to 5 kbar are applied to KBr, KCl and NaCl crystals containing U-centers, and the Grüneisen constant is calculated from the pressure induced shift of the local mode frequency. The experimental

Grüneisen constant for KBr is compared with the values calculated from several models of the U-center potential well, and the U-center anharmonicity determined in this fashion is nearly that of the KBr bulk crystal.

The hydrostatic pressure dependence of the KBr U-center phonon side bands is also measured. The side bands reflect structure in the phonon density of states of the crystal, and from the pressure dependent frequency shift of one side band the Grüneisen constant is determined for phonons in a limited region of the Brillouin zone. Good agreement is obtained between this value and previous theoretical calculations of the Grüneisen constant.

The far infrared absorption from 3 to 650 cm^{-1} of several polyamino acids is measured in solution and in the solid state. The far infrared absorption spectra of amino acids and short chain oligomers are extremely temperature dependent with the appearance of numerous narrow absorption lines at 4.2°K . These absorption lines broaden or disappear at 300°K or for absorption measurements on samples in solution indicating that these lines result from crystalline order.

For hexa-L-alanine or longer polymers, relatively broad nearly temperature independent far infrared absorption lines are observed, indicative of a lack of well defined crystal structure. This conclusion is

supported by our powder x-ray diffraction studies and the observation of little difference between the far infrared spectra of polymers in solution or in the solid state. The failure to observe the predicted low frequency far infrared longitudinal acoustic mode in α -helical poly-L-alanine is attributed to the disorder of the polymer.

CHAPTER I

INTRODUCTION

The far infrared absorption properties of two different types of solids are investigated. The first is the ionic alkali halide crystal containing U-center impurities in which manifestations of the anharmonic potential in the impurity induced absorption are examined. The second type of solid investigated is the covalently bonded polyamino acid. In this case measurements in the far infrared are performed to test the prediction of low frequency vibrational motions from harmonic normal mode calculations and to investigate the conformational dependence of the far infrared modes.

A. The U-Center Local Mode and Side Bands

Impurity induced absorption in the ultraviolet region associated with the H^- impurity was discovered in 1936.¹ This absorption was assigned to an electronic transition of the impurity and subsequently the H^- impurity was referred to as the U-center. The concept of modes of oscillation outside the vibrational frequency region of the perfect crystal was introduced theoretically by Lifshitz in 1943.² The predicted mode of vibration was localized in space and in 1960 Schäfer provided

experimental evidence for the existence of such "localized modes".³ Schäfer measured the impurity induced absorption in the 500 cm^{-1} region resulting from H^- impurities in several alkali halides. The light mass of the H^- impurity vibrates at more than twice the maximum phonon frequency and hence this mode is only coupled to the lattice vibrations by anharmonic terms in the crystal potential. Near the local mode absorption Schäfer also observed side band absorption. In 1965 Fritz identified these side bands as resulting from anharmonic processes in which creation or destruction of a lattice phonon is accompanied by excitation of the local mode.⁴

In addition to the presence of side bands, the temperature dependence of the local mode frequency and linewidth result from anharmonic coupling to the lattice phonons.⁵⁻⁷ The frequency of the local mode absorption shifts as a function of temperature and the linewidth of the local mode absorption increases as the temperature is increased. The observed temperature dependence of the linewidth has been compared with the dependence calculated from anharmonic interactions.^{6,8,9} However, because the linewidth is narrow at 4.2°K , accurate measurements are difficult at low temperatures. As an extension of previous work on the U-center we have measured the low temperature linewidth of U-centers in KCl and NaCl at higher resolution than previously available. In addition we report the first measurements on the KBr U-center line-

width for temperatures below 90°K and compare these measurements with theoretical predictions.⁹ When the theoretical linewidth is scaled by a factor of 6, good agreement is obtained between theory and experiment.

A different measure of the crystalline anharmonicity results from stressing the U-center crystals. Exerting pressure on a crystal changes the interionic distances resulting in a change in the potential interaction of the ions. Previous measurements of the uniaxial stress dependence of the U-center local mode frequency permit calculation of the hydrostatic pressure shift of the U-center.¹⁰ However these measurements involve strains which are an order of magnitude smaller than those obtained with readily available hydrostatic pressure techniques.¹¹ At hydrostatic pressures of several kilobars typical changes in the lattice constant of the KBr, KCl and NaCl crystals are on the order of 1% which allows accurate determination of the hydrostatic pressure shift. At these pressures large shifts in the frequency of impurity modes have been observed and off center impurities have been forced onto a regular lattice site.¹² In the case of the U-center local mode the hydrostatic pressure shift can be compared with the shift calculated from theoretical models of the U-center potential well to determine whether the anharmonic content of the models is correct. The U-center anharmonicity in KBr determined in this fashion is found to be nearly that of the bulk crystal.

In addition to measuring the hydrostatic pressure shift of the U-center local mode frequency, we have measured the hydrostatic pressure dependence of the KBr U-center side bands. The side bands reflect structure in the phonon density of states and from one feature in the side bands it is possible to deduce the anharmonic pressure dependence of phonons in a limited region of the Brillouin zone.^{13,14} This information can then be used to check the anharmonic content of the bulk lattice potential models used to describe these phonons.¹⁵ The quantity which describes this anharmonicity is the Grüneisen constant γ . The experimental and theoretical values of the Grüneisen constant agree to within the experimental error of the measurements.

B. Normal Modes of α -Helical Polypeptides

After fifteen years of studying the conformation of peptide chains using x-ray techniques, Pauling and Corey in 1951 proposed the α -helical structure for polypeptides.¹⁶ Subsequent studies in the 1500 to 3000 cm^{-1} region revealed shifts of the higher frequency modes associated with different conformations of the polymers.¹⁷ The far infrared absorption features of biopolymers remained unstudied until 1966 when Peticolas and Dowley speculated on the possibility of observing the low frequency oscillations of homopolymers.¹⁸ In an effectively one dimensional calculation with bonding between an

amino acid and its nearest and third nearest neighbor amino acid residues, the dispersion curve was found to obey the relation

$$\omega = 2[\omega_1^2 \sin^2(\frac{\varphi}{2}) + \omega_3^2 \sin^2(\frac{3\varphi}{2})]^{\frac{1}{2}}$$

where ω is the frequency, φ is the phase between nearest neighbor residues and ω_1^2 and ω_3^2 characterize the nearest and third nearest neighbor bond strengths respectively. Such low frequency acoustic modes are of particular interest since they may be associated with the helix-coil transition. This transition is of importance in understanding the conformation of proteins which are complex compared to homopolymers.

Since the suggestion of the possibility of observing low frequency oscillations in biopolymers, several experimental and theoretical investigations have been undertaken.¹⁹⁻²³ The simplest biopolymer assuming an α -helical structure is poly-L-alanine (PLA). The vibrational dispersion curves of PLA have been calculated and extend from 0 to 3000 cm^{-1} . The higher frequency curves show little phase dependence and only small frequency shifts associated with conformational changes.²³ Since lower frequency modes involve cooperative motion of the α -helix, they are sensitive indicators of the polymer conformation. The absorption lines observed in infrared spectra of polymers correspond to the $\vec{k} = 0$ (dipole active) vibration of the transverse optic mode of thin alkali halide

films.^{24,25} In 1968 Shimanouchi and Itoh measured the far infrared absorption of PLA to $\approx 80 \text{ cm}^{-1}$ and later obtained satisfactory agreement in comparing their measurements to calculations of the expected infrared active modes.^{19,20} In 1969 Raman measurements on PLA revealed modes of even symmetry.^{21,22} These measurements were all at frequencies higher than the expected acoustic oscillations. However, Raman data on another polymer poly(hydroxybutylglutamine) suggested the possibility of observing low frequency absorption in complex polymers.²⁶

We have measured the far infrared absorption of several polymers in solution and the solid state from 3 to 650 cm^{-1} . In most of these samples the expected low frequency acoustic structure is not observed. This result is explained in terms of intermolecular disorder which has the effect of broadening the low frequency modes of the polymers being studied.

C. Plan of the Thesis

Chapter II of this thesis describes the experimental far infrared techniques used in these studies. For the U-center investigations a grating monochromator was used coupled with a Ge:Cu photodetector. For the biopolymer measurements interferometers were used with low temperature Ge:Ga bolometer detectors.

In Chapter III measurements on the U-center crystals are reported. The temperature dependence of the local mode linewidth in KBr, KCl and NaCl is measured. The shift of the local mode frequency as a function of hydrostatic pressure is also measured for these crystals. In addition the hydrostatic pressure dependence of the KBr U-center side bands is observed. The results of these experiments are compared to theoretical predictions.

In this chapter the possibility of observing the U-center Zeeman effect is considered. This observation is not as trivial as predicted in the literature, but it is still within the realm of possibility with existing experimental techniques.²⁷ The Zeeman effect of the U-center is a direct measure of the effective charge of the H^- impurity.

In Chapter IV measurements on polyamino acids are reported. The far infrared spectra of several polymers are observed under varying conditions. The spectra are measured in the solid state at 300°K and 4.2°K and in solution. The effect of variation in polymer composition on the far infrared spectra is also investigated. The spectra of several proteins are measured for comparison with the homopolymer spectra.

Appendix A involves measurements on gap modes in KI and on Tl^+ impurity induced absorption in RbI and RbBr. The linewidth of gap modes in KI is estimated and compared with experimental measurements. The broad impurity

induced absorption in RbI and RbBr is expected to be indicative of the density of states of the pure crystal.^{14,28}

In Appendix B far infrared measurements on miscellaneous organic compounds are reported. The observed features are consistent with the interpretation that crystalline structure is necessary to obtain narrow far infrared absorption lines.

Some of the subject matter of this thesis has been presented at an American Physical Society Meeting²⁹ and is discussed in several papers.³⁰⁻³²

CHAPTER II

EXPERIMENTAL FAR INFRARED TECHNIQUES

The U-center local mode absorption is one of the narrowest lines occurring in solids. For example the KCl U-center absorption which occurs at 500 cm^{-1} is only 0.14 cm^{-1} wide at 4.2°K . To investigate the low temperature linewidth of this absorption, a high resolution spectrometer was needed. The resolution was provided by double passing the grating of a monochromator and thereby doubling the dispersion of the grating. To take advantage of this increased resolution it is necessary to maximize the detector performance. Although it does not respond for energies less than the acceptor energy gap ($\omega \equiv 1/\lambda \equiv 1/\text{wavelength} \approx 300\text{ cm}^{-1}$), a Ge:Cu photodetector provides optimum performance in the 500 cm^{-1} region. Its noise is determined by the fluctuations in the number of photons absorbed by the detector and under these circumstances the detector is said to be in the BLIP condition (background limited infrared photodetector). Hence a reduction in the number of photons hitting the detector will result in a better signal to noise ratio and enable us to take advantage of the high resolution monochromator.

The absorption features of the biopolymers on the other hand are quite broad, and because of the complexity

of these samples, they have many absorption lines in the infrared. In the 2 to 200 cm^{-1} region in the spectrum of poly-L-alanine there are four lines which are at least 20 cm^{-1} wide even before polarization studies to separate out the different symmetries of overlapping lines. To investigate biopolymers in the far infrared, Fourier transform spectroscopy was used. Fourier transform techniques allow the observation of the entire spectral region of interest at all times instead of just the single resolution width which can be observed at any given time with a monochromator. This multiplex or Fellgett advantage results in an improvement in the signal to noise by the square root of the number of resolution widths in the observed spectrum for equal times of observation of the same spectral region.³³ Since the photodetector does not permit measurements at energies less than the impurity level energy gap, a different detection apparatus was used for the low frequency measurements on biopolymers. Bolometers were used which respond uniformly to all infrared wavelengths by the heating and cooling of the detector element.

A. Monochromator

1. Prism Fore Optics

Figure 2-1 shows a diagram of the grating spectrometer and prism fore optics used in the measurements on the U-center. The prism fore optics is used as a wide

Spex 1500-II Spectrometer

Prism Fore Optics

Figure 2-1. Double-pass monochromator and prism fore optics apparatus showing the globar source (S), prism (P), chopper (C), grating (G), entrance slit(S_1), exit slit(S_2), and mirrors ($M_1 - M_9$). Mirrors 8 and 9 are on the top half of the median plane and provide for the second pass of the grating.

band-pass filter to eliminate the overlapping orders which would be a problem later in the grating section of the machine. The source, prism and mirrors 1, 2, and 3 are components from a Perkin-Elmer Model 98 monochromator. The global source is operated in the power dissipation range of 150 to 200 watts and the corresponding global temperature determined with an optical pyrometer is in the 1300°K to 1400°K range. At the high end of this power range the global tends to degrade over a period of several weeks of continuous operation while using lower power levels prolongs the life of the global.

Infrared radiation from the source is collimated by an off-axis paraboloid (mirror 1) onto the prism. Either a KBr or a CsI prism was used to pre-filter the radiation depending upon the wavelength region of interest. After passing through the prism once the radiation is reflected by mirror 2 for a second pass of the prism and then the filtered radiation is focused by mirror 1 and plane mirror 3 onto the chopper. Rotation of mirror 2 results in scanning different wavelengths. The Perkin-Elmer components are arranged in a Littrow geometry so that scanning different wavelengths does not result in changing the position of the image on the chopper.³⁴ If the prism pre-filtering mode of operation is not desired, the radiation can be intercepted before the prism by a reststrahl filter or by a plane mirror and reflected back to mirror 1 to be focused on the chopper.

The 18 blade mechanical chopper is belt driven by a synchronous motor and results in a chopping frequency in the 400 to 1300 Hz range. The reference signal for the lock-in amplifier is provided by a photodiode which detects chopped light from a reference lamp. The reference circuit is shown in Figure 2-2. 110 VAC is rectified and filtered to provide a stable DC voltage for the reference lamp. Further filtering yields a very stable DC voltage which is applied to the photodiode and the reference input. This filtering against 60 Hz results in a stable, though slightly rounded (because of the response time of the photodiode), square wave reference signal.

After being chopped the infrared radiation is focused onto the bottom half of the entrance slit by mirror 5 and enters the grating part of the monochromator as shown in Figure 2-1. The prism fore optics vacuum container has multiple connectors for electrical feedthroughs as well as ports for taking the radiation out of the system in a vertical or horizontal direction from the exit slit of the grating monochromator.

2. Spex 1500-II Double-Pass Grating Monochromator

The grating monochromator used in the U-center measurements is a Czerny-Turner type monochromator.³⁴ Mirrors 6 and 7 can be thought of as portions of the same spherical mirror (as in an Ebert-Fastie system) so there is a central axis of symmetry for these mirrors

Figure 2-2. Prism fore optics reference circuit for 1 kHz operation.

down the center of the monochromator. Hence for high resolution measurements (200 μ slit widths at $\lambda = 20 \mu$) curved slits on loan from Dr. T. Timusk are used so that the distance from the axis of symmetry to the slit is a constant which allows the focus of the system to be adjusted for all points on the slit. For lower resolution measurements the distortion resulting from using straight slits is not important.

The radiation that enters the lower half of the entrance slit is dispersed by the grating. A resolution bandwidth would leave the top half of the exit slit except that it is intercepted by mirrors 8 and 9 and sent through the system for a second pass of the grating. The doubly dispersed radiation then exits the grating monochromator at the bottom half of the exit slit and returns to the prism source box. Here the radiation can be directed vertically or horizontally out of the fore optics chamber into a detection cryostat.

Figure 2-3 shows the optical path of a single-pass grating monochromator in more detail. Evaluation of the optical path lengths gives constructive interference for

$$n\lambda = 2d \sin \theta \cos \phi$$

where n is the order of the interference and d is the spacing of the grating lines. Since $\lambda \propto d$, the infrared wavelengths can be determined from the standard counter wavelength (where $\lambda = 0$ is determined from scanning

Figure 2-3. Enlargement of a single-pass monochromator used in calculating the resolving power.

zeroth-order) and grating line spacing to be 3×10^{-3} $\mu/\text{\AA}$ where $\text{\AA}$ are the counter units and the infrared grating used (on loan from Dr. T. Timusk) has 40 lines/mm. This relation was verified by comparing the observed wavelengths of water vapor lines in the 20 μ region with other measurements of these wavelengths.³⁵

Differentiating the above equation gives

$$nd\lambda = 2d \cos \theta \cos \phi d\theta$$

A resolution width is determined by rotation of the grating through a small angle $d\theta$ resulting in movement of the image center from one side of the exit slit to the other side as shown in Figure 2-3. The slit-width determined resolution derives from $d\theta = S/2f$ where S is the slit width and f is the focal length. In double-pass operation the dispersion of the system is doubled so $d\theta = S/4f$ and

$$\frac{\lambda}{d\lambda} = \frac{4f}{S} \tan \theta$$

is the slit-width limited resolving power.

The ultimate diffraction limit of the resolution in double-pass is given by two times the usual result. That is, $\lambda/d\lambda = 2nN$ where N is the number of rulings on the grating, and an advantage of the double-pass system is that a larger diffraction limited resolving power is obtained. In addition when the system is operating in

single-pass the slit-width limited resolution can only be doubled by halving the slit width of both the entrance and exit slits resulting in a factor of four decrease in the signal level. If the double-pass mode is used instead of changing the slit width, a slight loss occurs on the second pass because of the grating efficiency which is almost one near the blaze.³⁴ In addition the doubled dispersion means that half as much radiation makes it out of the exit slit. Hence the net loss in signal is only slightly more than a factor of two for twice the resolution.

It is difficult to examine the resolving power of the system experimentally near the diffraction limit because of the relatively small signal levels involved. It is possible, however, to examine the consequences of operating near the diffraction limit by measuring the half-width of zeroth-order radiation. In zeroth-order no dispersion is present since the grating acts like a mirror and some care must be taken in applying the resolution formulas. Considering the grating to be replaced by a mirror, one finds the half-width $\Delta\theta$ is given by

$$\Delta\theta = \frac{S}{4f} \approx \sin(\Delta\theta) = \frac{\Delta\lambda}{2d}$$

where $\cos \varphi \approx 1$, $\Delta\theta$ is small and $\Delta\lambda$ is a counter reading and does not correspond to any dispersion. Hence

$$\Delta\lambda_s = \frac{Sd}{2f}$$

is the slit-width determined half-width. The diffraction determined resolution width for an aperture of width D is

$$\Delta\varphi = \frac{\lambda/2}{D} = \frac{\lambda}{2Nd} = 2\Delta\theta = \frac{\Delta\lambda}{d}$$

where $\lambda/2$ is the retardation for each of the two passes of the aperture. Hence the diffraction width is

$$\Delta\lambda_D = \frac{\lambda}{2N}$$

for the Rayleigh criterion. Here $\lambda \approx 20 \mu$ is a measure of the average wavelength transmitted by the system.

The appropriate way to combine these two widths is to convolute the triangular slit function with the diffraction function $(\sin(x)/x)^2$, as in Reference 36. The convoluted resolution is derived for the Spex from these calculations by noting that the slit determined resolution width is the same for the Spex in double-pass as in the calculated case but the diffraction limited resolution width is here a factor of two smaller than that quoted in the article. Redefining the slit resolution width to be a factor of two greater relative to the diffraction limit results in replacing δ by 2δ in the expressions of Reference 36 where δ is related to the slit width by $\delta = (S/2f)/(\lambda/D)$. The convoluted resolution width $\Delta\lambda$ is then given by

$$\frac{\Delta\lambda}{\Delta\lambda_D} = 2\delta + h(2\delta)$$

where 2δ expresses the slit resolution width at slit width $2S$ and $h(2\delta)$ is the corresponding broadening due to diffraction. This result is the dashed line plotted in Figure 2-4. The points shown in the Figure are the measured values, and the solid line shows the result of a Gaussian combination of the diffraction resolution width and the slit determined half-width

$$\frac{\Delta\lambda}{\Delta\lambda_D} = \left[\left(\frac{\Delta\lambda_S}{\Delta\lambda_D} \right)^2 + 1 \right]^{\frac{1}{2}}$$

The difference between the Gaussian and the convolution calculations is only a couple of percent. The correct functional form is observed when the resulting curves are compared to the experimental data. However, at larger slit widths there is an error of about 10% indicating that perhaps there was an error in the slit width of this amount.

Since measurements on the U-center crystals with the monochromator yield intensity as a function of wavelength, a convenient way of extracting the observed half-alpha points of the lines was needed. The intensity at the peak of the absorption is $I = I_0 \exp(-\alpha_0 t)$ where α_0 is the absorption constant and t is the crystal thickness. The intensity I' at the half-alpha point is given by

$$\frac{I'}{I_0} = e^{-\alpha_0 t/2} = \sqrt{I/I_0}$$

so

$$I' = \sqrt{II_0}$$

Figure 2-4. Comparison of measured resolution width of double-pass monochromator (points) with values calculated from a convolution (dashed line) and Gaussian combination law (solid line).

gives the intensity at the half-alpha points. This calculation gives the experimental linewidth but the broadening due to the instrumental resolution must still be extracted. The earlier success of the Gaussian combination law in combining the diffraction and slit limited resolution widths suggests that the Gaussian combination law be applied here. Indeed various checks were made to insure that the extraction procedure was accurate including checks for self consistency at different slit widths (e.g. 200, 400 and 800 μ) and comparison with half-widths measured with Dr. H. Gush's high resolution interferometer.³⁷

The actual extraction procedure involves measuring the width of the zeroeth-order peak. Then the angular dependence is introduced to calculate the half-width at some nonzero grating angle θ . For larger slit widths where diffraction is not important, this amounts to multiplying the zeroeth-order width by $\cos \theta$. The final linewidth $d\lambda$ was then calculated using the Gaussian combination law

$$d\lambda^2 = d\lambda_0^2 - d\lambda_I^2$$

where $d\lambda_0$ is the observed half-width and $d\lambda_I$ is the instrumental resolution width at angle θ . At 4.2°K the values obtained in this fashion for the KCl and NaCl linewidths agreed quite well with those measured at 0.023 cm^{-1} resolution with H. Gush as shown in Table 2-1.

The 0.023 cm^{-1} resolution width was also extracted using a Gaussian combination law (see Appendix A).

TABLE 2-1

Comparison of Measurements of 4.2°K U-Center Linewidths

Crystal	$\Gamma \text{ (cm}^{-1}\text{) Spex}$	$\Gamma \text{ (cm}^{-1}\text{) Gush}$
KCl	0.142	0.138
NaCl	0.164	0.175

3. Charcoal Vacuum Pump

The prism fore optics and the grating monochromator form a common vacuum chamber. Since no windows are needed between these systems, there are no losses caused by vacuum windows. A diagram of the cold trap and the charcoal pump used in evacuating this system is shown in Figure 2-5. The two liter charcoal section is evacuated at room temperature and then operates as a sorption pump for air at liquid N_2 temperatures. The charcoal pump does not have the vibrational problems of a mechanical pump and the liquid N_2 dewar is large enough so that the pump can be left unattended for a week at a time. In practice the monochromator vacuum system is first roughed down to several hundred microns with a mechanical pump. The mechanical pump is then valved off and detached and the

Figure 2-5. Cryogenic charcoal sorption pump and cold trap used to evacuate monochromator.

charcoal pump is opened to the monochromator. Pressures of less than 10 microns have been maintained for two weeks and the experiments have always been completed before the two liters of charcoal saturate.

B. Ge:Cu Detector and Cryostat

Figure 2-6 shows the detector cryostat used in the linewidth measurements on the U-center. After leaving the spectrometer exit slit, the infrared radiation enters the light pipe through a cold baffle. The cold baffle and light pipe can be cooled by conduction to less than 140°K using a liquid nitrogen cold trap which lowers the background flux of photons incident upon the detector from room temperature radiation. The light pipe is $\frac{1}{2}$ " ID brass that has been cleaned and then polished in a lathe with Wenol polish to provide for better transmission of the 500 cm^{-1} ($20\text{ }\mu$) infrared radiation. A 4 mil thickness of clear polyethylene separates the spectrometer and cryostat vacuum chambers. The outer diameter of the polyethylene is squeezed between two flanges covered with a thin layer of vacuum grease and this arrangement is vacuum tight even at liquid nitrogen temperatures.³⁰

The infrared radiation proceeds down the light pipe and through a sample mounted on a temperature controlling ring. A $1\text{ k}\Omega$ ($\frac{1}{8}$ watt) Allen-Bradley carbon resistor calibrated with a 100 Ω Electric Thermometers Inc. platinum resistor was used to determine the temperature of the

Figure 2-6. Ge:Cu detector cryostat for 4.2°K operation with liquid nitrogen cooled light pipes to reduce background radiation flux.

sample to an accuracy of better than 1%. The resistances were measured on a Keithley resistance bridge with lead compensation. A three point calibration was used to interpolate temperatures between 10°K calibration intervals and temperatures were controlled by an Artronix temperature controller.³⁸⁻⁴⁰ After the sample the radiation proceeds through an OCLI Ge interference filter and then via a light cone into a 3/8" diameter spherical integrating cavity. In the condensing cone the beam diameter is reduced from 1/2" to 3/32" and the angle of radiation making a 5° angle with respect to the light pipe axis is increased to 90°. ⁴¹ Since the conical half-angle of radiation coming from the Spex is roughly 4°, relatively few glancing reflections occur proceeding down the light pipe, and this results in a higher transmission of the light pipe system than if many bounces occurred.

The Ge:Cu photodetector used in the measurements on the U-center samples was supplied by Dr. J. R. Houck. The detector material was fabricated by diffusing copper into high purity germanium at high temperature and then quenching the crystal rapidly. A chip of this material was obtained from Dr. Houck, and after etching the detector, leads were attached with indium solder. The ground lead was a copper strip to provide a heat sink for the detector. There are three acceptor levels that are introduced into the band gap of germanium by the copper impurity. The lowest level of 0.04 eV $\approx$ 300 cm⁻¹

is the interesting level for our measurements. At temperatures below 15°K this level is essentially unpopulated unless radiation with $\omega > 300 \text{ cm}^{-1}$ is incident on the detector. This detector has the advantage of being relatively fast having a hole lifetime of 3×10^{-7} sec which permits the use of AC detection techniques in the kilocycle region limited only by the RC time constant of the detector and leads.⁴²

A convenient quantity used to characterize the detector performance is the noise equivalent power (NEP). The NEP is the incident photon signal power at which the signal to noise ratio of the detector is unity. In our case 20 μ radiation was chopped at 500 Hz and conversion was made to a standard 1 Hz electronics bandwidth in the calculations. Since the signal and noise are equal, the NEP is also a measure of the noise and decreasing the NEP results in less noise. To check the performance of the monochromator, the light pipe system and the detector, three calculations of the NEP were performed for the light pipe at 300°K. In the first, estimates are made of the signal power throughput of the monochromator and light pipe system. The second and third involve calculating the fluctuations resulting from the background power of photons incident on the detector.

From the power output of the global source and the transmission of the monochromator and light pipe system it is possible to estimate the NEP of the Ge:Cu detector.

The black body radiation in a wavelength interval $d\lambda$ from a source of area A at a temperature T can be calculated using the formula

$$P_{\lambda} = B_{\lambda} A d\lambda d\Omega$$

where $d\Omega$ is the solid angle of radiation collected and

$$B_{\lambda} = \frac{hc^2}{\lambda^5 (e^{c_2/\lambda T} - 1)}$$

is the power per unit area, per unit solid angle and per unit wavelength.⁴³ Here c is the speed of light and h is Planck's constant. At 20μ and 1300°K with $c_2 = 1.44 \text{ cm}^\circ\text{K}$ we find

$$B_{\lambda} = 2.5 \times 10^{-3} \text{ w/cm}^2\text{-}\mu\text{-sr}$$

For $\frac{1}{2}$ " high slits with a width of 0.25 mm , $A = 3.2 \times 10^{-2} \text{ cm}^2$ and $d\lambda = 3.5 \times 10^{-3} \mu$. Since $D = 10.2 \text{ cm}$ and $f = 81 \text{ cm}$, $d\Omega = (D/f)^2 = 1.6 \times 10^{-2} \text{ sr}$ and

$$P_{\lambda} = 4.5 \times 10^{-9} \text{ w}$$

To convert to an AC RMS power one multiplies this by $\frac{1}{2}$. At this power level a signal to noise ratio $S/N = 40$ was observed where $\Delta f = 1/8\tau = 0.125 \text{ sec}^{-1}$ was the frequency bandwidth of the detection electronics determined from the PAR lock-in time constant τ . Dividing $\frac{1}{2}P_{\lambda}$ by S/N and $\sqrt{\Delta f}$ yields

$$\text{NEP} = (1.6 \times 10^{-10} \text{ w}) \mathcal{T}_1 \mathcal{T}_2 = 5.5 \times 10^{-12} \text{ w}$$

where $\mathcal{T}_1$ and $\mathcal{T}_2$ are the transmission of the optics and cryostat respectively as given in Table 2-2.

TABLE 2-2

Transmission of Monochromator and Cryostat

Transmission of monochromator

global emissivity ⁴⁴	0.8
fore optics magnification	0.7
grating efficiency ³⁴	0.8
<hr/>	
total	0.45 = $\mathcal{T}_1$

Transmission of cryostat

light pipe (4' long with a right angle bend) and condenser	0.2
Ge filter (L155009 from OCLI)	0.55
integrating cavity efficiency	0.7
<hr/>	
total	0.08 = $\mathcal{T}_2$

In Table 2-2 the cavity efficiency expresses the fact that some of the radiation entering the integrating cavity is lost back out the hole or to absorption in the walls.^{45,46} This is expressed by a formula which gives the fractional number of photons incident on the detector as

$$\frac{A_D}{(A_D + A_H + A_w \frac{8R}{3R_o})} = 0.7$$

where A_H is the area of the hole, A_w is the area of the cavity walls, $A_D = 0.16 \text{ cm}^2$ is the active area of the detector, $R = 1.2 \Omega$ is the surface impedance of the brass cavity at 20μ and $R_0 = 377 \Omega$ is the impedance of free space.

The NEP of the detector also can be calculated from the fluctuations in the background power incident upon the detector. We have

$$\text{NEP} = 2 \left(\frac{P_b h c \omega \Delta f}{\eta} \right)^{\frac{1}{2}}$$

where P_b is the background power and $\eta \approx 0.4$ is the quantum efficiency of the detector.^{42, 47} For $\omega \approx 500 \text{ cm}^{-1}$ and a 1 Hz bandwidth

$$\text{NEP} = 3.2 \times 10^{-10} (P_b)^{\frac{1}{2}} \text{ watts}$$

where P_b is in watts.

To calculate the NEP we must estimate the background power incident upon the detector. Using standard tables for 300°K radiation one finds that in the 16 - 30 μ region

$$P_b = 1.3 \times 10^{-2} \text{ w/cm}^2 \left(\frac{d\Omega}{2\pi} \right) A \mathcal{T}_2$$

where $d\Omega = \pi \langle \theta^2 \rangle$. Here $\langle \theta^2 \rangle = 3.6 \times 10^{-2} \text{ rad}^2$ is a measure of the angle of collection of the detection system determined by observing the AC signal from a hot soldering iron as the soldering iron is moved so that

different angles of radiation are collected. Using the area of the $\frac{1}{2}$ " diameter light pipe as the collection aperture for black body radiation from the room, one finds

$$P_b = 2.4 \times 10^{-5} \text{ watts}$$

and then

$$NEP = 1.6 \times 10^{-12} \text{ watts}$$

The background power can be estimated in a different fashion using the AC responsivity of the detector. A blackened beaker of liquid nitrogen was chopped with a blackened chopper blade directly in front of the light pipe with a $\frac{1}{4}$ " diameter baffle to attenuate the signal. The background power P_b used above divided by 8 (a factor of 2 to convert to AC RMS and a factor of 4 from the aperture change) gives an AC responsivity

$$S = 8.3 \times 10^4 \text{ v/w} = 1.3 \text{ a/w}$$

where the biased detector resistance was 64 k Ω . The bias circuit is shown in Figure 2-7. A typical bias voltage was 25 v/cm and the AC responsivity determined above compares well with the value of 1 a/w measured by Quist at this bias voltage.⁴² The DC voltage across the detector was 4.6 v and this voltage is a measure of the carriers generated by the background photon flux. Hence we estimate

Ge:Cu Bias Circuit

InSb Bias Circuit

Figure 2-7. Detector bias circuits. Top: Ge:Cu bias circuit used to apply 25 v/cm to the detector at 4.2°K. Bottom: InSb bias circuit used to apply 1 ma to the detector (the detector, bias resistors and transformer are at 4.2°K).

$$P_b = \frac{V}{R} = 5.5 \times 10^{-5} \text{ w}$$

and then from the BLIP condition

$$\text{NEP} = 2.4 \times 10^{-12} \text{ watts}$$

Hence the three estimates of the NEP agree to within a factor of three.

The preceeding calculations were for the case that the light pipe system was at 300°K. Cooling the light pipe and baffles to less than 140°K results in a decrease in the area of collection of 300°K radiation by a factor of 0.15 and a decrease in the solid angle by a factor of 0.62. Hence the background power is down by a factor of 0.093 and the detector resistance with the NaCl crystal in the beam was observed to change from 120 kΩ to 2 MΩ which is roughly the factor of 10 increase expected. As predicted by the BLIP expression the factor of 10 decrease in the background power resulted in the signal to noise improving by a factor of 3. Hence

$$\text{NEP} \approx 1 \times 10^{-12} \text{ watts}$$

with the light pipe cold. Using the Ge interference filter also decreased the background power by a factor of 10 and hence the total improvement in signal to noise over the non-cold filtered case was a factor of 10.

C. Pressure Cell and Detector Insert

The pressure cell insert used in the hydrostatic pressure measurements on the U-center is shown in Figure 2-8. The apparatus used to pressurize the He gas that constitutes the pressure transmitting fluid was constructed by Fulton and Fitchen and has been described elsewhere.^{11,12} Commercially bottled He gas is raised in pressure from 2,000 psi to 20,000 psi and stored in a portable cart. The cart has an intensifier and hydraulic pump to further pressurize the gas to a maximum of 135,000 psi. The hydrostatic pressure is determined from a resistance bridge and the relation $P = 0.885 \Delta R$ for a Harwood man-ganin gauge.

Since the rate of pressurization and depressurization is critical for the Si pressure windows used in the 500 cm^{-1} frequency region, the pressure cart was modified by replacement of the electrical hydraulic pump with a hand hydraulic pump.⁴⁸ This system allowed the pressure to be raised at less than the 10 bar/sec prescribed rate. Slow decreases in the pressure were accomplished by opening one of the pressure connectors slightly so that a small leak occurred. Pressures of up to 5 kbar (1 bar = 0.9869 atm) were obtained and the temperature of the pressure cell was maintained at 40°K to ensure that the He^4 in the cell was in the fluid phase and had not solidified.

Figure 2-8. Pressure cell and detector insert used in the hydrostatic pressure measurements.

After taking some precautions to minimize attenuation of the signal, a factor of 50 loss in signal was observed on inserting the pressure cell in place of a section of light pipe. A factor of 4 was lost at each Si window and the remaining factor of 4 was lost in traversing the rest of the cell. Hence the largest losses resulted from the necessity of using Si as the window material. Unfortunately with the possible exception of diamond, Si is the most transparent material capable of easily withstanding pressures of 5 kbars. Because of these losses, it was necessary to use 2 mm monochromator slit widths in the pressure measurements instead of the 0.2 mm slit widths common in the linewidth measurements.

The polycrystalline Si windows used in these measurements were cylinders $\frac{1}{4}$ " in diameter by $\frac{1}{4}$ " high. These windows were glued to the polished surface of mushroom plugs that seal under pressure by the extrusion of indium.¹¹ The mushroom plugs have threads in their central bore for extraction. Two mil polished brass shim stock bent in the form of a cylinder was used to cover these threads and increase the transmission of infrared radiation. The light cones used in these measurements were made from beryllium copper and condense the beam diameter from $\frac{1}{8}$ " to the $\frac{3}{32}$ " mushroom plug aperture. These cones cause little loss in signal with two cones back to back transmitting 80% of the radiation that a straight light pipe transmits. The samples are mounted inside a small

polished brass cylinder which has an inner diameter of 0.2" and fits inside the sample chamber.

After the radiation leaves the pressure cell, it proceeds into the detector section of the cryostat. The outer detector chamber vacuum window is a 1/16" thick Ge window which has been soldered with indium into a 5 mil walled section of the brass light pipe.³⁰ Except for near the vacuum window, the light pipe wall thickness is 1/32". Next the radiation goes through the Ge interference filter and on into the condenser and integrating cavity.

Because of the low level of the background power which makes it to the detector, the detector resistance is greater than 100 M Ω , and caution must be exercised to use as short leads as possible to keep the associated RC time constant small. Typical frequencies of operation were 400 Hz, and though there was some damping of the signal by the RC time constant, the detector noise was attenuated by the same amount. Furthermore preamplifier noise was not important since the noise level was substantially smaller at zero bias than with 25 v/cm and the detector noise increased as the bias was increased. Sources of noise that increase in this fashion are photon noise and current noise.^{49,50}

D. Interferometers and Ge:Ga Bolometers

In the measurements on biopolymers interferometers

were used with bolometer detectors since the region from 2 to 700 cm^{-1} was under investigation. This apparatus has been described elsewhere so only a brief outline of its performance will be given here.⁵¹⁻⁵⁴ The Michelson interferometer is shown at

the right with monochromatic radiation of frequency ω_0 incident on the beam splitter

(BS). After the beam is divided, the separate parts travel to different mirrors (M_1, M_2) and then are recom-

bined at the detector (D). A cosine interference pattern in the intensity as a function of path difference x between the two arms of the interferometer results. Fourier transforming the intensity as a function of distance gives the spectral information which in this case is a delta function at frequency ω_0 . In general the spectral information contains a broad band of frequencies determined by the beam splitter efficiency and the filtering but Fourier transform techniques again yield the spectral content of the interferogram (intensity as a function of x). The Fellgett advantage then results from the observation of all frequencies at all times in the interferogram.³³

The Michelson interferometer is used in the high frequency region since the mylar beam splitting efficiency

is adequate for $\omega > 30 \text{ cm}^{-1}$. In the lower frequency region a lamellar interferometer is used which provides a different means of splitting the beam. A set of interleaved metal plates divide a plane wave so that the distance traveled by half the wave (reflected by one set of plates) is different than that traveled by the other half (reflected by the other set). An interferogram results as the flat surface of one set of plates is displaced with respect to the other set of plates. This interferometer was used down to 2 cm^{-1} where the source intensity is quite weak.

The power from a black body source $P_{\omega} \propto \omega^2 \Delta\omega$ in the long wavelength region of the far infrared so more sensitive detectors were needed with the lamellar than with the Michelson interferometer. In the higher frequency region a detector system with a Ge:Ga bolometer operating at pumped He^4 temperatures was used. In the low frequency region a Ge:Ga bolometer in a more complex pumped He^3 system was used since the detector noise is smaller at 0.3°K than 1.2°K and the responsivity of the 0.3°K detector is greater. That is, the resistance as a function of temperature is steeper. The interferometer and detection apparatus used in the different frequency regions is shown schematically in Figure 2-9.

The Michelson interferometer was modified to provide for measurement of frequencies up to 1000 cm^{-1} . For this purpose a $1/8$ mil beam splitter was used. Since

EXPERIMENTAL SETUP

Figure 2-9. Schematic representation of interferometer and bolometer use in different frequency regions.

the mylar vibrates like a drum head, mechanical vibrations are a problem and care was taken to eliminate vibrations caused by the mechanical chopper. A commercially available Aerotec translational stage was inserted in place of the machine screw and stepping motor to improve the accuracy of the step length. The minimum step length of the new stage is 1/10 mil. To maintain the state of interference of the system for discrete sampling techniques, one requires that the step length be accurate to about 5% and that the translating mirror remain parallel to the zero path difference position to a similar degree of accuracy.

The accuracy of the stepping motor has been examined by translating the fixed mirror so that the zero path difference point occurs at a different position in the travel of translational stage. To within the signal to noise, the zero path difference (ZPD) amplitude remained unchanged indicating that the translating mirror remains parallel to the original zero path difference position. There was a 10% variation (as a percentage of the ZPD intensity) in the intensity of the points nearest the ZPD point after adjustment of the fixed mirror so that the intensity level before ZPD equalled the level after ZPD. Using the interferogram scanning function^{55,56}

$$I(x) = I_0 \frac{\sin x}{x}$$

we find

$$\frac{dI}{I_0} = \frac{dx}{x} \quad \text{at } x = \pi .$$

So the resultant percentage error in the step length is also 10%. The maximum error contributed by the stepping motor is given as 5% by the manufacturer which is the correct order of magnitude to explain the observed variation. Additional errors might be contributed by the drive mechanism of the translational stage.

E. InSb Electron Bolometer

The electron bolometer consisting of n-type InSb was described by Kinch and Rollin in 1963.⁵⁷ This detector has the advantage of being fast with a response time $\tau = 3 \times 10^{-7}$ sec and has a NEP at 4.2°K of 3×10^{-13} watts which is of the same order of magnitude as that of a pumped He⁴ cooled detector. The electron bolometer operates on the principle of heating and cooling of the electrons rather than of the entire lattice as is the case for Ge bolometers. At 4.2°K n-type InSb of high purity has a high carrier mobility or, equivalently, a low effective mass. Hence the carrier phonon coupling is weak and it is possible to modulate the effective temperature of the electrons which are uncoupled from the lattice.

The electron bolometer performance is limited to low frequencies. If τ_s is the scattering time for free carriers, the classical formula for the conductivity is

$$\sigma = \sigma_0 / [1 + (2\pi c)^2 \omega^2 \tau_s^2]$$

where σ_0 is the DC conductivity. Now $\tau_s \approx 3 \times 10^{-13}$ sec, so the absorption which is proportional to σ is constant until $\omega \tau_s \approx 1/2\pi c$ or $\omega \approx 20 \text{ cm}^{-1}$ and then decays as $1/\omega^2$ to higher frequencies. Because of this limitation in the detector absorption, the electron bolometer was useful only for $\omega < 40 \text{ cm}^{-1}$ with the lamellar interferometer. The detector parameters are given in Table 2-3. Six 2 mil diameter gold leads were attached to the detector with indium solder.

TABLE 2-3

Properties of Single Crystal n-Type InSb Detector

dimensions	160 x 160 x 20 mils
resistivity	0.099 - 0.110 Ω -cm
Hall mobility	$7.0 - 7.5 \times 10^5 \text{ cm}^2/\text{v-sec}$
carrier concentration	$8.1 - 8.4 \times 10^{13}/\text{cm}^3$ at 77°K

This detector is a low impedance device so some care must be taken in matching the impedance to an AC lock-in amplifier. The detector chamber in the lower portion of the cryostat in Figure 2-6 provided enough room for cooled circuitry (transformer and bias resistors). The circuit used with InSb is shown in Figure 2-7. The JAF 2 transformer has a 45 dB shield which is important

in reducing pickup from stray electromagnetic fields. The noise level using unshielded transformers was roughly a factor of two worse than with the JAF 2. The $10\ \Omega$ resistor in the primary loop serves to divert some current from the low resistance primary coil to the detector.⁵⁸ The fractional increase in Johnson noise ($\propto \sqrt{R}$) one would expect from the $10\ \Omega$ resistor was 20%, however, detector noise was predominate since increasing noise was observed with increasing current.

In operation the detector was biased with a current of 1 ma. The JAF 2 transformer has ± 3 dB frequency response from 100 to 15,000 Hz so the AC detection frequency used was 200 Hz. A tuned secondary was not needed since the parallel combination of the secondary impedance of the transformer ωL_s and the transformed detector impedance $R_D n^2$ is already $\approx R_D n^2$ where n is the turns ratio of the transformer. A PAR lock-in with type D preamp was found to have a sufficiently low noise level not to contribute significantly to the noise of the detector. Though the signal is somewhat less than that observed with a 1.2°K Ge:Ga detector system, the noise is also smaller. The resultant signal to noise ratio was of the same order of magnitude as that for a pumped He^4 system in which the detector response was limited by cold filters to the low frequency region of the far infrared.

F. Cells for Solution Studies

Several different cells for containing liquids were used in the studies of polypeptides in solution. The cell used depended upon the solvent being used and the frequency region under investigation. The two basic cell designs are shown in Figure 2-10.

Since water absorbs strongly in the far infrared spectral region ($\alpha \approx 200 \text{ cm}^{-1}$ at $\omega = 20 \text{ cm}^{-1}$), a cell was needed with a path length of solution of less than 0.01 cm. The cell we used is shown in the top half of Figure 2-10. A 1, 2 or 4 mil spacer which is squeezed between two crystal quartz windows seals in the solution and this spacer also determines the thickness of the solution. To prevent leakage of infrared radiation around the water in the center of the cell, 1/32" thick black rubber washers were placed between the quartz windows and the brass cell frame. Radiation passing through the teflon spacer around the solution is then intercepted and absorbed by the black rubber. The brass cell frame is counter bored to hold the black rubber and the quartz windows. The assembled cell is shown in the Figure. Care must be taken to avoid trapping air bubbles in the solution section during assembly of the cell.

Since chloroform is more transparent than H_2O in the far infrared ($\alpha \approx 20 \text{ cm}^{-1}$ at $\omega = 20 \text{ cm}^{-1}$), a thicker spacer can be used for studies involving chloroform. A 1/32" or 1/16" teflon spacer was used in the cell shown

✓

Brass Cell Frame

Figure 2-10. A brass cell frame and two assembled cells (a and b) used in solution studies.

in the top half of Figure 2-10. Two small holes at the top of each of these spacers permit the cell to be filled or emptied with a hypodermic syringe. After the cell is filled, these holes are plugged with stainless steel wires to prevent evaporation of the solution.

Benzene and carbon tetrachloride are even more transparent than chloroform in the far infrared ($\alpha \approx 2 \text{ cm}^{-1}$ at $\omega = 20 \text{ cm}^{-1}$) so solution samples up to 1 cm in length were used in studies involving these solvents. The cell used for these solutions is shown in the bottom half of Figure 2-10. To allow measurements at higher frequencies than with the cells discussed previously, $\frac{1}{2}$ mil teflon windows were used. $\frac{1}{32}$ " teflon washers assist in sealing the teflon windows against the pyrex tube. The assembled cell is shown in the Figure. This cell is filled and emptied with a pipette, and a stopper prevents evaporation of the solvent.

CHAPTER III

U-CENTERS IN KBr, KCl AND NaCl

A. Crystal Preparation

Pure single crystals of KBr, KCl and NaCl were grown for these studies by the Cornell Materials Science Crystal Growing Facility. These crystals were additively colored as shown in Figure 3-1.^{59,60} As depicted in the top half of the Figure, potassium metal was placed under vacuum in a pyrex tube containing the alkali halide crystals. The end of the pyrex tube nearest the potassium metal was sealed off. Then the potassium was distilled into the crystal section by successively heating the bulbs at the left and sealing these sections off at the constrictions after each section was emptied of potassium. After the potassium has been distilled in this fashion into the crystal section of the tube, the constriction nearest the vacuum pump is sealed off creating the bob shown in the bottom half of the Figure.

Coloration of the crystals is then accomplished by differentially heating the bob. The cold end of the bob at temperature T_1 determines the potassium vapor pressure, while the warm end containing the crystals at temperature $T_2 = 600^\circ\text{C}$ allows the potassium vapor to color the crystals uniformly by the diffusion of F-centers (e^-)

Figure 3-1. Additive coloration of alkali halide crystals. Top: Distillation of potassium metal. Bottom: Coloration of the crystals by F-centers.

throughout the crystals. The concentration of the F-centers is determined by the vapor pressure and hence is dependent on T_1 . After roughly an hour of maintaining temperatures T_1 and T_2 , the crystals are quenched rapidly to room temperature by removing the bob from the furnace and cooling it with compressed air.

The F-centers that result from these coloration procedures are subsequently converted to U-centers by heating the crystals under a pressure of 10 atm of hydrogen in a stainless tube. The time t_3 and temperature T_3 required for this conversion process were determined by trial and error. Table 3-1 lists the conditions used for several of the U-center crystals.

TABLE 3-1

U-Center Crystal Preparation Conditions

Lot No.	Crystal	$T_1(^{\circ}\text{C})$	$T_3(^{\circ}\text{C})$	$t_3(\text{hour})$
2	KBr	250	350	$\frac{1}{2}$
2	KCl	250	375	$\frac{1}{4}$
2	NaCl	250	550	$\frac{1}{8}$
3	KBr	300	350	1
5	KCl	400	440	2
5	NaCl	400	590	1

The concentration of U-centers in the Lot No. 2 crystals can be estimated from a graph of the concentration of F-centers in a KBr crystal versus the concentration of potassium atoms in the vapor.⁶⁰ At 250°C the potassium vapor pressure of 6.6×10^{-5} atm results in a density in the gas of 6.6×10^{14} /cc at the hot end of the coloration bob. Assuming complete conversion of F-centers to U-centers in the subsequent heating operation, the concentration of U-centers can be estimated from the above mentioned graph to be 2×10^{15} /cc. Similarly, since at 300°C the potassium vapor pressure is five times the 250°C value, the concentration of U-centers at 300°C can be estimated to be 1×10^{16} /cc. Although these calculations used data applicable to KBr, comparable concentrations of U-centers are expected for KCl and NaCl U-center crystals with similar absorption strengths since the U-center oscillator strengths of all these crystals are comparable.

The crystals containing lower concentrations of U-centers (Lot No. 2) were used in the temperature dependent linewidth studies. One-eighth inch thick Lot No. 2 samples absorbed $\approx 50\%$ of the incident radiation at the peak of the local mode absorption using high resolution (resolution width $\approx 2.8 \times 10^{-3}$ μ). In the hydrostatic pressure measurements on the U-center local mode, ten times lower resolution was used and more absorption strength was needed to make the local mode observable.

Roughly ten times the absorption strength was obtained by using the Lot No. 3 and No. 5 crystals listed in Table 3-1 in 1/8" thick and 1/16" lengths respectively. For the U-center side bands to be observed, even higher U-center concentrations were necessary. For measurements on the side bands Dr. T. Timusk supplied a 0.2" thick KBr crystal with 6×10^{17} U-centers/cc.

B. Hydrostatic Pressure Measurements

1. Local Mode Frequency Shift in KBr, KCl and NaCl

Applying hydrostatic pressure to the U-center crystals changes the interionic spacing of the crystals. The resultant shift in the local mode frequency is indicative of the anharmonic content of the potential seen by the U-center. Measurements on the local mode frequency shifts of KBr, KCl and NaCl were performed simultaneously with all three of these crystals in the pressure cell. Pressures up to 5 kbar were obtained with the sample temperature being maintained at 40.8°K. The resolution used in these measurements was 0.03 μ . The frequency shift as a function of pressure is shown in Figure 3-2. As indicated in the Figure, straight lines fit the data to within the error in the frequency determination which is roughly the size of the experimental points. In fact this data could be used as a calibration of a new hydrostatic pressure gauge. A U-center crystal could be included in a sample chamber with other crystals under investigation

Figure 3-2. Hydrostatic pressure dependent shift of the KBr, KCl and NaCl U-center local mode frequencies.

and the hydrostatic pressure shift of the U-center frequency could be used to determine the pressure. This would be particularly useful for low temperature studies in which the He pressure transmitting fluid is solidified. The pressure could be determined to better than 1% by this procedure using the data in Figure 3-2 and higher resolution studies of the U-center frequency shift could allow an accuracy of 0.1% to be achieved.

The hydrostatic pressure coefficient A_1 describes the shift of the U-center frequency ω_0 as a function of pressure. From Figure 3-2 we find

$$A_1 = 4.30 \pm 0.01 \text{ cm}^{-1}/\text{kbar for KBr}$$

$$A_1 = 3.80 \pm 0.01 \text{ cm}^{-1}/\text{kbar for KCl}$$

$$A_1 = 2.67 \pm 0.01 \text{ cm}^{-1}/\text{kbar for NaCl} .$$

The hydrostatic pressure coefficient (A_{1g} symmetry compression) for KCl U-centers can be compared with the value calculated indirectly from uniaxial stress measurements for stresses nearly an order of magnitude smaller than those of the hydrostatic measurements. For a uniaxial stress S

$$A_1 S = \Delta\omega_0(\parallel) + 2\Delta\omega_0(\perp)$$

where $\Delta\omega_0(\parallel)$ and $\Delta\omega_0(\perp)$ are the frequency shifts for the electric field vector parallel and perpendicular to the [100] crystal symmetry direction of the applied stress.⁶¹

From the data of Fritz et al.¹⁰

$$A_1 = 4.2 \text{ cm}^{-1}/\text{kbar for KCl}$$

Our determination of the hydrostatic pressure coefficient agrees with this value to within the quoted 10% accuracy of the uniaxial stress measurements.

a. Grüneisen Constant for KBr, KCl and NaCl

The Grüneisen constant γ is a dimensionless number used to describe potential anharmonicity as defined by the expression

$$\gamma \equiv - \frac{d}{d} \frac{\ln \omega_0}{\ln V} = \frac{1}{\omega_0 \chi} \left(\frac{\partial \omega_0}{\partial P} \right)_T$$

where measurements are performed at constant temperature, V is the crystal volume and χ is the bulk crystal compressibility. The first portion of this expression allows the Grüneisen constant to be calculated from theoretical models of the dependence of frequency on interionic spacing. The last part of this expression permits calculation of the Grüneisen constant from experimental determinations of the frequency shift as a function of pressure. Using extrapolated values of the low temperature compressibility given by Sharko and Botaki, we find

$$\gamma = 1.63 \pm 0.01 \text{ for KBr}$$

$$\gamma = 1.54 \pm 0.01 \text{ for KCl}$$

$$\gamma = 1.21 \pm 0.01 \text{ for NaCl}$$

where $\chi = 5.90 \times 10^{-3}/\text{kbar}$ for KBr, $\chi = 4.93 \times 10^{-3}/\text{kbar}$ for KCl and $\chi = 3.93 \times 10^{-3}/\text{kbar}$ for NaCl.⁶²

As a first approximation, the Grüneisen constant can be calculated from the Ivey rule

$$\omega_0 d^x = \text{const.}$$

where d is the lattice constant and the parameter x gives the frequency dependence of the U-center for different alkali halides. This relation can be applied directly to the case of the hydrostatic pressure shift of the ultraviolet absorption of the U-center.⁶³ In the case of the local mode the situation is more complex. For the alkali halides under consideration here, changing the alkali metal constituent results in $x = 1.1$ while changing the halogen component results in $x = 2.2$.⁶⁴ This difference is much larger than that expected from changing the nearest neighbor mass of the U-center and probably involves differences in relaxation of the lattice around the U-center. These values of x give an average Grüneisen constant $\gamma = x/3 = 0.55$ which is smaller than the experimentally determined Grüneisen constants by a factor of 3. A similar discrepancy was observed in the case of the ultraviolet absorption and differences between the local and bulk compressibility were invoked to partially explain this result.⁶³

The Grüneisen constant for U-centers in KCl can also be estimated from the change in the lattice parameter and

the associated frequency shift of the local mode resulting from the inclusion of Rb^+ impurities in KCl .⁶⁵ The Grüneisen constant calculated in this fashion is 1.1 which is still 30% smaller than the value determined from our hydrostatic pressure measurements on KCl .

b. Model Calculation of the Grüneisen Constant for KBr

The Grüneisen constant has been defined as a bulk property involving the experimentally determined frequency shift and volume change of the bulk crystal. However, theoretical calculations of the pressure dependent frequency shift involve the change in volume associated with the U-center. The potential seen by the U-center can be written as an expansion of the nearest neighbor potential interaction with the harmonic terms in the expansion determining the U-center local mode frequency. Hence in this model the nearest neighbor separation is important in determining the U-center frequency.

Assuming that the lattice transmits the applied pressure to the nearest neighbors, we are interested in how much the nearest neighbors collapse and the associated volume change dv . This collapse can be estimated from calculations of the force constants ($K(A_{1g})$ for pure KBr and $k(A_{1g})$ for the U-center) which resist A_{1g} symmetry compressions of the nearest neighbors. From the relation

$$K(A_{1g})dV = k(A_{1g})dv$$

we find

$$\gamma = - \frac{K(A_{1g})}{3k(A_{1g})} \frac{d \ln \omega_0}{d \ln a'}$$

where a' is the nearest neighbor separation for the U-center. Quantum mechanical calculations of these force constants for 1.5% nearest neighbor relaxation in KBr give

$$K(A_{1g})/k(A_{1g}) = 1.15$$

where $k(A_{1g}) = K_1 + K_2 = 29,120$ dyne/cm and $K(A_{1g}) = 2K_1^0 + 4K_{\perp}^0 = 33,560$ dyne/cm.⁶⁶ Born and Huang have shown that the compressibility of a crystal is inversely proportional to a force constant of the crystal.⁶⁷ Since the compressibility involves an A_{1g} symmetry compression and the above force constants express the resistance to such stresses, the ratio of these force constants is an estimate of the ratio of the bulk to local compressibility.

The ratio of the compressibilities calculated in this fashion is considerably different from the ratio of the T_{1u} force constants. In the case of KBr the correct U-center frequency is obtained for a 60% relaxation of nearest neighbor force constants at the impurity site, and the ratio $K(T_{1u})/k(T_{1u})$ is 2.5.⁶⁴ The difference in the A_{1g} and T_{1u} force constant ratios is not terribly surprising considering the different symmetries involved

in determining these force constants and analogous results have been obtained in calculations of the F-center local compressibility.^{63,68}

Using the Grüneisen constant formula for KBr in the form

$$\gamma = -0.384 \frac{d \ln \omega_0}{d \ln a}$$

it is possible to examine the anharmonic content of several heuristic models of the U-center potential well that have been used to calculate the KBr U-center frequency.

These models start with a two body model of the KH potential similar to that shown at the right. For small separations there is a hard repulsive core and for larger separations there is a weak attractive contribution to the potential.

In the models discussed here the repulsive core is represented by a Huggins-Mayer potential

$$U_{HM} = \lambda e^{-r/\rho}$$

where λ and ρ are parameters and the weak attractive potential is represented by the Van der Waals interaction⁶⁹

$$U_{VW} = \frac{-C}{r^6} - \frac{D}{r^8}$$

where

$$C = \frac{3h}{2} \frac{\nu_1 \nu_2}{\nu_1 + \nu_2} \alpha_1 \alpha_2$$

and

$$D = \frac{9hC}{4e^2} \left[\frac{\nu_1 \alpha_1}{p_1} + \frac{\nu_2 \alpha_2}{p_2} \right]$$

Here 1 and 2 refer to the two atoms involved, ν is the series limit of the discrete spectra of the ion, α is the crystal polarizability of the ion, p is the number of valence electrons in the outer shell, h is Planck's constant and e is the electronic charge.

This potential function is then expanded about the equilibrium positions of the atoms in the crystal. In the case of the U-center in KBr there are six nearest neighbors whose contribution to the potential seen by the U-center must be considered. The force constant determined for the U-center in this fashion is⁶⁹

$$k = \lambda e^{-a'/\rho} \left[\frac{2}{\rho^2} - \frac{4}{\rho a'} \right] - \frac{60C}{(a')^8} - \frac{112D}{(a')^{10}}$$

and the frequency of the local mode is

$$\omega_0 = \sqrt{k/m}$$

where m is the H^- mass, $C = 3.46 \times 10^{-59}$ erg-cm⁶ and $D = 6.38 \times 10^{-75}$ erg-cm⁸. This expression for the frequency can be used to calculate the Grüneisen constant. In the literature there are several different values of

λ and ρ used to determine the frequency of the local mode and calculation of the Grüneisen constant enables a choice to be made between these models on the basis of anharmonicity. The frequency and Grüneisen constant are given in Table 3-2 for two different models of the potential with relaxation δ of the nearest neighbors of the U-center between 0 and 4%.

TABLE 3-2
Model Calculations of ω_0 and γ for
U-Centers in KBr

$\delta(\%)$	$a'(\text{\AA})$	$\omega_0(\text{cm}^{-1})^*$	γ^*	$\omega_0(\text{cm}^{-1})^{**}$	γ^{**}
0	3.266	399	1.83	516	0.852
1	3.233	419	1.81	528	0.834
2	3.200	439	1.78	540	0.815
3	3.167	461	1.76	551	0.796
4	3.134	483	1.74	563	0.776

*Parameters of Reference 70.

**Parameters of Reference 69.

The results in Table 3-2 can be compared with the experimental values $\omega_0 = 446 \text{ cm}^{-1}$ and $\gamma = 1.63$. The best agreement with the experimental results is obtained with the first calculation shown in the Table with 3% nearest neighbor relaxation. The parameters used in this calculation were $\lambda = 1.269 \times 10^{-9} \text{ erg}$ and $\rho = 0.3394 \text{ \AA}$ where ρ

is the KBr bulk crystal value. As might be expected, the rapid variation of the exponential in the Huggins-Mayer potential dominates the Van der Waals term in determining the Grüneisen constant. While putting $C, D = 0$ has a 10% effect on the frequency, it only has a 2% effect on the Grüneisen constant.

In the second model in Table 3-2, parameters were used that were determined from Raman scattering measurements with $\lambda = 1.213 \times 10^{-10}$ erg and $\rho = 0.594$ Å being the values which fit the data of Reference 69 at 2% nearest neighbor relaxation. The calculated frequency is 10 to 20% too large although inclusion of an additional polarizability term used in the potential model of Reference 69 results in the calculated frequency being 10% too small. This additional term has a disastrous effect on the Grüneisen constant, changing the result at 2% nearest neighbor relaxation from 0.815 to 0.654. The calculated values of the Grüneisen constant using this model are too small to account for the observations, indicating that this potential does not have sufficient anharmonic content.

Since C and D have only a 2% effect on the Grüneisen constant in the first model, a simple analytical expression can be obtained by setting these constants equal to zero and solving for γ in terms of ρ . We have⁷¹

$$\begin{aligned}\gamma &= \frac{1.15}{3} \frac{a'}{\omega_0} \frac{d\omega_0}{da'} \\ &= \frac{1.15}{6} \frac{a'}{k} \frac{dk}{da'} \\ &= \frac{1.15}{6} \left[\frac{\sigma^2 - 2\sigma - 2}{\sigma - 2} \right]\end{aligned}$$

where $\sigma = a'/\rho$. Solving for σ at 2% nearest neighbor relaxation using $\gamma = 1.63$ gives $\rho = 0.365 \text{ \AA}$ which is only 8% larger than the KBr bulk crystal value used in the first model calculation. However this value is significantly smaller than the $0.580 \text{ \AA}$ used in the Raman model calculation or the value $0.4724 \text{ \AA}$ determined from the KH molecular interaction.⁷² Since the harmonic force constants are different for the different symmetry motions involved in the U-center infrared and Raman active modes, it is not unexpected that the anharmonic contribution to these force constants should be different.⁶⁶

c. Lattice Strain Correction

In the preceeding sections the Grüneisen constant was calculated using the bulk compressibility to express the lattice strain as a linear function of hydrostatic pressure. However at higher pressures a quadratic correction must be included so the lattice strain is then given by

$$\frac{a - a_0}{a_0} = - \frac{\Delta a}{a_0} = C_1 P - C_2 P^2$$

where $C_1 = x/3$ at 41°K is determined from low temperature compressibility data, C_2 is measured at 300°K and a_0 is the nearest neighbor spacing at zero pressure.^{62,73} The constant C_2 is only weakly temperature dependent and in any event at pressures of 5 kbar only a small correction results from this term for the alkali halides being considered. The resultant equations relating the pressure in units of kbar and the percent strain are

$$-\frac{\Delta a}{a_0} = 0.1967 P - 0.0036 P^2 \text{ for KBr}$$

$$-\frac{\Delta a}{a_0} = 0.1643 P - 0.0026 P^2 \text{ for KCl}$$

$$-\frac{\Delta a}{a_0} = 0.1310 P - 0.0018 P^2 \text{ for NaCl}$$

Since expansions of the potential are used to calculate the force constant, it is convenient in graphical representations to express the frequency shift in terms of the force constant change $\Delta k/k_0$ where k_0 is the U-center force constant at zero pressure. Figure 3-3 shows the percent change in the force constant as a function of the percent lattice strain. The data shown indicate that the force constant change has both a linear and quadratic strain dependence given by

$$\frac{\Delta k}{k_0} = -c_1 \left(\frac{\Delta a}{a_0} \right) + c_2 \left(\frac{\Delta a}{a_0} \right)^2$$

Assuming the local and bulk strains have similar pressure

Figure 3-3. Force constant change as a function of lattice strain for KBr, KCl and NaCl U-center local modes.

dependence, c_1 and c_2 are indicative of the expansion of the anharmonic U-center potential. Table 3-3 lists the values of these parameters for $\Delta k/k_0$ and $\Delta a/a_0$ expressed in percent. Using the above relation to calculate the Grüneisen constant of the U-center local modes for small strains, one finds $\gamma = c_1/6$ which gives $\gamma = 1.64 \pm 0.03$ for KBr, $\gamma = 1.56 \pm 0.03$ for KCl and $\gamma = 1.22 \pm 0.03$ for NaCl. These values agree with the Grüneisen constants calculated earlier from the graph of the local mode frequency shift versus pressure.

TABLE 3-3

U-Center Anharmonic Potential Parameters
for KBr, KCl and NaCl

Crystal	c_1	c_2
KBr	9.84 ± 0.2	1.25 ± 0.2
KCl	9.34 ± 0.2	1.02 ± 0.2
NaCl	7.34 ± 0.2	0.71 ± 0.2

2. U-Center Side Band Frequency Shift in KBr

The measurements on the U-center local mode absorption yield information about the anharmonicity of the potential seen by the U-center.^{4,6,7} Similarly, hydrostatic pressure measurements on the U-center Stokes side bands provide information about the anharmonicity of the

pure crystal potential. The Stokes side bands correspond to the simultaneous excitation of the U-center local mode at frequency ω_0 and lattice phonons at frequency ω_i . In the first approximation, neglecting symmetry considerations, the Stokes side band absorption at frequency $\omega = \omega_0 + \omega_i$ is proportional to $\mathcal{D}(\omega_i)/\omega_i^3$ where $\mathcal{D}$ is the phonon density of states of the pure crystal.⁸ Hence peaks in the phonon density of states can result in absorption peaks in the side band spectrum, and measuring the hydrostatic pressure dependence of the U-center side bands allows us to deduce the pressure dependence of structure in the density of states.

The experimental arrangement was similar to that used in the pressure measurements on the local mode frequency. The sample temperature was maintained at 40.8°K while a hydrostatic pressure of up to 5 kbar was applied. Because of the loss of a factor of 50 on traversing the pressure cell, the slit width determined resolution was limited to 0.09 μ . At that resolution it was still necessary to smooth the noise observed on the data. Data was recorded on chart paper and later the smoothed data was digitized for analysis. The pressure cell was disassembled between the runs of the pure and doped crystals needed to obtain the absorption constant. Hence the absolute accuracy of the absorption constant is limited by this sample change. More precise measurements of the side band absorption constant at zero pressure using

higher resolution have been reported previously.^{74,75}

Figure 3-4 shows the side band absorption of KBr crystals containing 6×10^{17} U-centers/cc at various pressures. The KBr U-center local mode absorption shifts to higher frequencies as pressure is applied, so measurements of the frequencies of the shifted side band structure were made relative to the shifted local mode absorption at that pressure. Points A through D were all observed to shift to higher frequencies with respect to the U-center line as the pressure was increased. Points B through D are indicative of the shifts of their neighboring maxima and can be determined more readily than the peak positions because of the breadth and overlapping of the peaks. The noise which shows up in the data as oscillations on peak A also complicates the determination of peak position. At higher pressures the relative shapes of the side bands remained unchanged except for a slight decrease in the height of the maximum near B. There is possibly a slight increase in the height of the peak near C although the noise makes this determination difficult.

The peak near B is of particular interest since in contrast to the other structure in the side band spectrum, it derives from a localized region of the Brillouin zone which in this case occurs at a saddle point at $[0.6, 0.6, 0]$ on the longitudinal acoustic branch (third-highest acoustic band).^{13,14} Furthermore, this peak position is insensitive

Figure 3-4. Hydrostatic pressure dependence of the KBr U-center side band absorption spectrum. Points A - D identify structure in the side bands.

to changing the U-center force constant relative to the pure crystal force constant.⁷⁴

Figure 3-5 shows the pressure dependent shift of the frequency of the various side band points with respect to the U-center frequency. As before we can define a Grüneisen constant to describe the anharmonicity of the crystal

$$\gamma = - \frac{d \ln \omega_i(\vec{k})}{d \ln V} = \frac{1}{\omega_i} \chi \left(\frac{\partial \omega_i}{\partial P} \right)_T$$

where χ is the bulk compressibility and measurements are performed at constant temperature. In a simple calculation this constant is the same for all phonons. In this model the value of γ measured for the points shown can be compared with the experimental and calculated values for the transverse optic mode.⁷¹ These results are shown in Table 3-4. The position of the broad peak A is difficult to determine so only an approximate value of the Grüneisen constant is given in the Table. For comparison, the average value of γ determined from thermal expansion data is 1.43.⁶⁷

A detailed calculation in three dimensions for the phonon spectrum results in different Grüneisen constants for different regions of $\vec{k}$ -space. Using a shell model potential adjusted to fit neutron scattering data, Cowley and Cowley have calculated the Grüneisen constant for KBr in different symmetry directions of the Brillouin zone.¹⁵

Figure 3-5. Hydrostatic pressure dependent shift of the KBr U-center side band points A - D.

TABLE 3-4

Grüneisen Constants of Features in the KBr U-Center
Side Bands and of the Transverse Optic Mode

Point	$\omega(\text{cm}^{-1})$ at $P = 0$	γ
A	43.9	0.9
B	76.8	1.93 ± 0.1
C	90.5	1.38 ± 0.1
D	106.6	1.46 ± 0.1
TO (exp.) ⁷¹	116	2.83 ± 0.1
TO (theory) ⁷¹		2.6

Their calculated value for the [0.6, 0.6, 0] saddle point is ≈ 1.76 for model A and ≈ 1.91 for model B which includes Coulomb interactions. The corresponding value of 1.93 ± 0.1 we have measured agrees well with the value from the more complete model B.

C. Temperature Dependence of the Local Mode Linewidth

1. Adjustable Parameter Models for KBr, KCl and NaCl

A different manifestation of the anharmonicity of alkali halide crystals involves the linewidth of the U-center.^{6,8,9,64} The U-center linewidth results from anharmonic coupling to the phonons of the bulk crystal. Two types of anharmonic interactions are important in

describing the linewidth. One involves the scattering processes which predominate at temperatures where the lattice phonon states are populated and the other concerns the decay processes which determine the linewidth at low temperatures.⁷⁶ These interactions are shown diagrammatically at the right

with the U-center represented by solid lines and the phonons by wavy lines. The scattering

process shown at the top results in annihilation of one phonon (wave vector $\vec{k}$) and creation of another ($\vec{k}'$), and

hence a change occurs in the

lattice vibrational environment of the U-center. In the decay process shown at the bottom, three lattice phonons are necessary to conserve energy. At low temperatures the U-center linewidth $\Gamma(0)$ is determined by the decay lifetime of the U-center. At higher temperatures the lifetime determined by scattering processes yields an additional contribution to the linewidth.

The scattering processes determine the lifetime of the original excited state $|\omega, n(\vec{k}), n(\vec{k}')\rangle$ by the transition to a new state $|\omega, n(\vec{k}) \pm 1, n(\vec{k}') \mp 1\rangle$ where n is the occupation number of the phonon states. Two types of terms coupling these states in the Hamiltonian are treated by perturbation theory and result in contributions of the

same order of magnitude to the relaxation time. The anharmonic terms that are important contain the operator dependence

$$\mathcal{K}_4 \sim (b + b^\dagger)^2 (a(\vec{k}) + a^\dagger(\vec{k}))(a(\vec{k}') + a^\dagger(\vec{k}'))$$

treated in the first order and

$$\mathcal{K}_3 \sim (b + b^\dagger)^2 (a(\vec{k}) + a^\dagger(\vec{k}))$$

treated by second order perturbation theory where the a's are the phonon and the b's are the U-center creation and annihilation operators. In the Debye approximation the corresponding linewidth is given by^{6,64}

$$\begin{aligned} \Gamma_{sc} &= \Gamma(T) - \Gamma(0) \\ &= \beta_c \left(\frac{T}{\theta_c} \right)^7 \int_0^{\theta_c/T} \frac{x^6 e^x dx}{(e^x - 1)^2} \rightarrow \begin{cases} T^2 (T \gg \theta_c) \\ T^7 (T \ll \theta_c) \end{cases} \end{aligned}$$

where β_c and θ_c are treated as adjustable parameters to fit the linewidth data.

A second model for the temperature dependence of the linewidth involves the assumption of coupling to a localized or resonant mode (Einstein oscillator) of energy kT_E instead of using the Debye density of states.⁷⁷ The expression for the scattering determined linewidth that results from the thermal occupation of the Einstein oscillator level is

$$\Gamma_{sc} = \beta_E \sinh^{-2}\left(\frac{T_E}{2T}\right) \rightarrow \begin{cases} T^2 & (T \gg T_E) \\ e^{-T_E/T} & (T \ll T_E) \end{cases}$$

In practice this relation and the previous one result in similar temperature dependence of the linewidth since $\Gamma(0)$ dominates the experimental linewidth before Γ_{sc} changes faster than T^3 . From the observed T^3 dependence, it is impossible to distinguish whether the ultimate functional form at lower temperatures would involve the seventh power of T or would have an exponential dependence on T . The log-log plot at the right shows the similar temperature dependence of the Debye (---) and Einstein oscillator (—) models.

The U-center linewidth as a function of T for KBr, KCl and NaCl crystals is shown in Figures 3-6 to 3-8. The crosses indicate higher temperature values taken from other measurements.^{5,78} The points represent our data with the error bars at low temperature resulting from variation in the measured values from run to run and from estimates of the accuracy of the spectrometer slit width extraction procedure. The accuracy of the temperature measurement is better than 1%. Each point on the graphs is an average of five consecutive spectrometer scans. Previous measurements on KCl and NaCl

Figure 3-6. Temperature dependence of the KBr U-center local mode linewidth.

Figure 3-7. Temperature dependence of the KCl U-center local mode linewidth.

Figure 3-8. Temperature dependence of the NaCl U-center local mode linewidth.

U-centers lacked the resolution of our measurements and consequently had much larger error bars for the low temperature linewidth.^{5,7} However the low temperature region is most sensitive to the value of θ_c or T_E since in that region the linewidth deviates from the T^2 behavior observed at higher temperatures.

The curves shown in Figures 3-6 to 3-8 indicate least mean square fits to the data by the Einstein oscillator density of states model. These fits of the data were easier to calculate than the nearly identical curves resulting from assumption of the Debye phonon model. In fact the Debye and Einstein oscillator model linewidth calculations overlap to within the thickness of the curves shown in the Figures. The effective temperature parameters for the two models are given in Table 3-5 along with the Debye temperatures θ_D resulting from specific heat measurements on the pure alkali halides. The θ_c values determined from the temperature dependence of the U-center linewidths are smaller than the corresponding Debye temperatures. This result is consistent with previous attempts at fitting U-center linewidth data.⁸ The disagreement could result from the simplifying assumption of the Debye model or from the assumption of uniform scattering by all the phonons. The calculated curves for KBr and KCl are good approximations of the observed data but in the case of NaCl the agreement between the calculated and observed linewidth is relatively poor. It is impossible to achieve

a good fit to the NaCl data at high temperatures since the linewidth varies more slowly than T^2 in that region.

TABLE 3-5

U-Center Linewidth Determined Effective
Temperature Parameters

Crystal	$\theta_D(^{\circ}\text{K})$	$\theta_C(^{\circ}\text{K})$	$T_E(^{\circ}\text{K})$	$\omega_E(\text{cm}^{-1})$
KBr	174	125	105	73
KCl	235	170	140	97
NaCl	321	175	145	101

The frequencies ω_E corresponding to the effective temperatures T_E are also shown in Table 3-5. Resonant or localized modes $\vec{k}$ and $\vec{k}'$ contributing to the Einstein oscillator model calculation of the U-center linewidth can be either both odd ($\mathcal{K}_4$ in first order) or both even ($\mathcal{K}_3$ in second order or $\mathcal{K}_4$ in first order). Far infrared spectroscopic studies are sensitive to the odd H^- impurity induced modes while Raman scattering studies are sensitive to the even impurity modes. Unfortunately the only Raman studies on U-centers in the 100 cm^{-1} region to our knowledge involved just KI.⁶⁹ However, even modes are also observed in the side bands of the U-center local mode although the amplitude of the side band features is increasingly attenuated the higher the frequency of

the even mode.

The ω_E values can be compared with the frequencies of the various observed modes. From far infrared measurements, resonances of the perturbed T_{1u} lattice modes occur at 88 and 99 cm^{-1} for U-centers in KBr and KCl respectively.^{14,79} Only a very broad absorption is observed in the far infrared spectrum of NaCl containing U-centers. In addition an E_g symmetry resonant mode is observed in the KBr U-center side bands at 80 cm^{-1} , and broad peaks in the U-center side bands of KCl and NaCl occur at 64 and 81 cm^{-1} respectively.^{74,75} Since the T_E parameters were only calculated to $\pm 5^\circ\text{K}$, $\omega_E = 73 \text{ cm}^{-1}$ is sufficiently close to the 80 cm^{-1} E_g mode frequency in KBr and $\omega_E = 97 \text{ cm}^{-1}$ is sufficiently close to 99 cm^{-1} T_{1u} mode frequency in KCl to suggest that coupling to these modes contributes significantly to the temperature dependence of the U-center local mode linewidth. No even or odd mode is observed close to $\omega_E = 101 \text{ cm}^{-1}$ for NaCl, and in any event the model calculations do not fit the NaCl temperature dependent linewidth data well.

2. Comparison of KBr Data with Gethins' Calculation

The discussion in the remainder of this section will be limited to the temperature dependence of KBr U-center linewidth. Previously there were no measurements of the linewidth in the temperature range below 90°K although the low temperature region is the most sensitive to changes in the temperature dependence of the linewidth.

Gethins has calculated the linewidth from parameters adjusted to fit the KBr U-center side bands in an anharmonic Green's function calculation.⁹ In this calculation the perturbed phonon density of states is used and there are no adjustable parameters. The resulting linewidth is a factor of 6 too small in the high temperature region and a factor of 3×10^3 too small at 4.2°K.

The discrepancy in the low temperature region can be attributed to broadening resulting from causes other than three phonon decay. There are several types of defects in the crystals that can cause broadening of the local mode absorption. Isotopes in the crystals change the effective mass and the frequency of oscillation of the local mode. Dislocations in the crystals result in changes in the U-center force constant and again the frequency of oscillation is affected. Finally, impurities (principally other alkali metals or halogens) cause both mass and force constant changes. Because of the availability of data on KCl, the calculations of the defect induced linewidth will be carried out on KCl although analogous results are expected for KBr and NaCl.

a. Isotope Induced Frequency Shift

An estimate of the isotope effect can be found by using the linear chain model. In this case the T_{1u} symmetry local mode corresponds to displacement of the H^- ion in one direction and of the K^+ nearest neighbors in the opposite direction

as shown in the diagram. The amplitude of the oscillation falls off exponentially with distance from the U-center and the reduced mass of the mode is

$$\frac{1}{\mu} = \frac{1}{m} + \frac{1}{2M}$$

where

$$\omega_0 = \sqrt{\frac{k}{\mu}} \approx \sqrt{\frac{k}{m}} \left(1 + \frac{m}{4M}\right)$$

and k is the nearest neighbor force constant. Taking differentials gives

$$\Delta\omega \approx -\omega_0 \frac{m}{4M^2} \Delta M$$

Changing the isotopic mass of one of the potassium nearest neighbors from 39 to 41 results in a change of -0.16 cm^{-1} in the local mode frequency. Changing the isotopic mass of both nearest neighbors results in a change of -0.32 cm^{-1} in the frequency. Since the potassium 41 isotope is 6.9% abundant, we would expect to observe three lines separated by 0.16 cm^{-1} from each other with integrated intensities in the ratio of 1:30:210.⁸⁰ The U-center local mode absorption constants for KBr at 4.2°K and KCl at 54.2°K as observed with the Spex are shown in Figure 3-9. The absorption constants of KCl and NaCl U-centers measured at 4.2°K with Dr. H. Gush's interferometer are shown in Figure 3-10. To within the accuracy of the measurements, no splitting or asymmetry that could

Figure 3-9. Lorentzian (dots) and Gaussian (crosses) fits to the 4.2°K KBr and 54.2°K KCl U-center local mode absorption data (solid lines).

Figure 3-10. Lorentzian (dashes) and Gaussian (solid lines) fits to the 4.2°K KCl and NaCl U-center local mode absorption data (dots).

be identified with the predicted isotope effect is observed in the local mode absorptions.

The central frequencies at 4.2°K of the KBr, KCl and NaCl U-center local mode absorption lines are given in Table 3-6. These values are taken from Figures 3-9 and 3-10 and other data. The 0.1 cm^{-1} difference between the frequencies measured with the Spex and those measured with Dr. Gush's interferometer may be attributed in part to cumulative scanning inaccuracies ($\pm 1.5 \times 10^{-3} \mu \approx \pm 0.03 \text{ cm}^{-1}$) in the Spex.

TABLE 3-6

4.2°K U-Center Local Mode Frequencies

Crystal	$\omega_0 (\text{cm}^{-1})$ Spex	$\omega_0 (\text{cm}^{-1})$ Gush
KBr	445.83	445.80
KCl	501.05	501.16
NaCl	562.21	562.31

A calculation of the isotope effect resulting from isotopic changes in the potassium nearest neighbors can also be made using a simple three dimensional model. This model results from a Green's function expansion for a mode in which the U-center moves in opposition to the six nearest neighbor potassium ions.⁸¹ The masses of

the pure crystal diatomic lattice are $M_1(\text{Cl}^-)$ and $M_2(\text{K}^+)$. The frequency at the top of the acoustic branch is $\omega_1 = \sqrt{6K/M_1}$ and the frequency at the bottom of the optic branch is $\omega_2 = \sqrt{6K/M_2}$ where K is the nearest neighbor force constant of the pure crystal. Equating the central and noncentral force constants of the diatomic lattice model of Mitani and Takeno results in the following expression containing the impurity mode frequency ω_0 :

$$y^2 B(y) = 1/\epsilon^*$$

where $y = \omega_0/\omega_1$ and $B(y)$ involves a Green's function of the unperturbed lattice.^{81,82} Expansion of the Green's function in the above equation for $y \gg 1$ gives

$$\begin{aligned} & \frac{y^2}{y^2 - 1} \left\{ 1 + [6(\alpha^2 y^2 - 1)(y^2 - 1)]^{-1} \right\} \\ &= \frac{1 + \lambda + \lambda(1 - \epsilon)y^2}{\epsilon(1 + \lambda) + \lambda(1 - \epsilon)y^2} \end{aligned}$$

where $\alpha = \omega_1/\omega_2$, $\lambda = (k/K) - 1$ and $\epsilon = 1 - (m/M_1)$.

Using $K = 3.39 \times 10^4$ dyne/cm and $k = 1.52 \times 10^4$ dyne/cm,⁶⁴ we find that changing the Cl^- mass from 35 to 37 has no effect on the frequency to 0.001 cm^{-1} . Changing the K^+ mass from 39 to 41 changes the local mode frequency by 0.058 cm^{-1} . Such a small isotope splitting would be unobservable in our measurements on the KCl U-center line which is already 0.14 cm^{-1} wide at 4.2°K . Also, since no asymmetry is observed in the U-center

absorption lines, the isotope effect cannot be contributing the major portion of the residual low temperature linewidths. The results of the isotope shift calculations for KCl are listed in Table 3-7.

TABLE 3-7

Calculated Isotope Shifts for U-Centers in KCl

$M_1(Cl^-)$	$M_2(K^+)$	$\omega_0 (cm^{-1})$
35	39	506.106
37	39	506.106
35	41	506.048

b. Dislocation Strain Broadening

A second type of defect that could contribute to the residual 4.2°K linewidths is the strain field resulting from dislocations. The effect of dislocations on paramagnetic resonances has been estimated previously for microwave experiments.⁸³ To estimate the number of dislocations in our crystals, we have used etch pit counting techniques.⁸⁴ To etch NaCl a solution of glacial acetic acid and 4% FeCl₃ was used, and for KBr and KCl an etch of propionic acid (H₂O free) with 2% BaCl₃ was used. The photographs of the etch pits which are reproduced in Figure 3-11 were made using a Reichert "Zetopan" microscope. In the photographs a 42.5 x 42.5 mm² square

Figure 3-11. Photographs of the etch pits (at magnification x425) used to determine the dislocation concentrations. KCl is shown in the top two photographs, KBr is shown at the bottom left and NaCl is shown at the bottom right.

corresponds to a $0.1 \times 0.1 \text{ mm}^2$ area of the sample. For NaCl and KCl there are $\approx 3 \times 10^6$ dislocations/cm² and for KBr there are $\approx 5 \times 10^6$ dislocations/cm².

The shear stress a distance r from a screw dislocation is

$$\sigma_{r\theta} = \frac{Gb}{2\pi r}$$

where for KCl $G = 1.19 \times 10^{11}$ dyne/cm² expresses the resistance to shear and $b = d/\sqrt{2}$ for face centered cubic crystals. Similar formulae result for edge dislocations. Setting the number of dislocations/cm² equal to $1/\pi r^2$, we estimate the average stress from dislocations to be $\langle \sigma_{r\theta} \rangle = 5.1 \times 10^6$ dyne/cm² for KCl. Using the KCl U-center hydrostatic pressure coefficient, the corresponding stress induced linewidth is 0.02 cm^{-1} (0.04 cm^{-1} for edge dislocations) which is small compared to the observed residual linewidth. Since impurities tend to congregate at the center of dislocations where the strain field is strongest, this calculation of the dislocation broadening might be an underestimate. However there is no evidence of concentration dependence of the U-center linewidth or of splitting of the U-center line caused by congregation of the H^- impurities. Annealing the crystals could be expected to decrease the dislocation counts by a factor of 10 and would result in an estimated broadening a factor of 3 smaller.

c. Impurity Strain Broadening

A combination of mass defect and force constant defect result from the inclusion of impurities in alkali halide crystals. The mass defect is only important for impurities close to the U-center as demonstrated in the isotope effect calculations. The strain field from an impurity of different size than the ion it replaces is a longer range effect in terms of contributing to the U-center linewidth. The effect of impurities on the linewidth can be estimated from measurements on Rb^+ impurities in KCl.⁶⁵ Empirically it was found that

$$\Gamma = A c^{\frac{1}{2}}$$

where $A = 3.1 \text{ cm}^{-1}/(\text{mole } \%)^{\frac{1}{2}}$ and c is the concentration of Rb^+ impurities. Assuming a similar formula holds for Na^+ impurities, 50 ppm Na^+ in KCl was estimated to result in a residual linewidth of 0.3 cm^{-1} .

The KCl U-center crystal used in our measurements has been analyzed by the Cornell Materials Science Center Analytical Laboratory. The crystal was found to have 1 - 10 ppm Na^+ , Rb^+ and F^- impurities and 10 - 100 ppm Br^- impurities. The relatively large Br^- concentration results from Br_2 that is a common contaminant in the Cl_2 gas under which the KCl crystals are grown.⁸⁵ Hence 50 ppm is the correct order of magnitude for the total alkali metal and halogen impurity level and, assuming the above empirical relation holds for all these impurities,

the estimated KCl residual 4.2°K linewidth is 0.3 cm^{-1} . This is the correct order of magnitude to account for the observed 0.14 cm^{-1} linewidth and dwarfs the other causes of linewidth that have been considered here. Other possible "impurities" besides the alkali metals or halogens, such as divalent ions or vacancies, are expected to be present in the crystals in lower concentrations. The highest purity crystals to be expected at the present time would have total alkali metal or halogen impurity levels of $2 \times 10^{-6} \text{ } \mu\text{g/g}$. The estimated linewidth in these crystals would be $\approx 0.06 \text{ cm}^{-1}$ assuming any other impurities introduced in the lengthy treatment of the crystal powder do not contribute to the linewidth significantly.⁸⁶

d. Comparison of R_2 Zero-Phonon and U-Center
4.2°K Residual Linewidths

Defects have also been suggested as the determining factor for the 4.2°K R_2 zero-phonon electronic transition linewidth.⁸⁷ The R-center consists of an aggregation of three F-centers (e^-) in three anion vacancies. From the defect induced strain, the Grüneisen constant allows us to estimate the resultant linewidths for the R_2 zero-phonon transition and for the U-center local mode. Consider first the model calculation of the Grüneisen constant for the phonons of a linear diatomic chain which gives⁸⁷

$$\gamma \equiv - \frac{d}{d} \frac{\ln \omega}{\ln a} = - \frac{a}{2K} \frac{dK}{da}$$

where a is the nearest neighbor separation. In this case since $\omega^2 = K/M_{\text{eff}}$ and since only M_{eff} varies for different phonons, the Grüneisen constant is the same for all the phonons. Hence for a given internal strain $\Delta\omega/\omega \propto \Delta a/a$ is the same for all phonons.

An analogous result is obtained in the case of the R- and U-centers. The frequency of the U-center vibrational and the R_2 zero-phonon electronic transition are approximately related by⁸⁸

$$\omega_R \approx \sqrt{\frac{m}{3m_e}} \omega_U$$

so that

$$\left(\frac{\Delta\omega}{\omega}\right)_U \approx \left(\frac{\Delta\omega}{\omega}\right)_R \propto \frac{\Delta a}{a}$$

as in the case of phonons treated above. From the data on the R_2 zero-phonon 4.2°K linewidth in KCl and from our data on the U-center 4.2°K linewidth in KCl we find $(\omega_0/\Gamma(0))_U = 3750$ and $(\omega_0/\Gamma(0))_R = 1850$. This is adequate agreement considering that crystals from different sources were used in these measurements and that the symmetries of the transitions involved have not been considered.

e. Extraction of the 4.2°K Linewidth

Since the residual low temperature linewidth of the

U-center is caused by strains instead of three phonon decay, it is necessary to extract the 4.2°K linewidth to compare the data with Gethins' theoretical predictions. For KCl and NaCl at 4.2°K, the lineshapes shown in Figure 3-10 are perhaps more Gaussian ($\alpha = A \exp[-(\omega - \omega_0)^2 \ln(2)/\Gamma^2]$) than Lorentzian ($\alpha = A/[(\omega - \omega_0)^2/\Gamma^2 + 1]$). However the KBr 4.2°K U-center absorption is definitely Lorentzian as shown in Figure 3-9. The data shown are the smoothed averages of three consecutive spectrometer scans. A. Hughes has predicted and observed the Lorentzian shape of the N₁-center zero-phonon line resulting from strain broadening although the strain field and distribution of impurities assumed in his calculations determine the form of the lineshape.⁸⁹ In Figure 3-9 the 54.2°K lineshape of the KCl U-center absorption is also shown to be Lorentzian. This broadened lineshape is determined by phonon scattering and a similar lineshape is expected for the KBr U-center absorption at similar temperatures.

Because the KBr U-center lineshape is Lorentzian, extraction of the residual linewidth as shown in Figure 3-12 is a simple procedure with $\Gamma_{sc} = \Gamma(T) - \Gamma(0)$ where $\Gamma(T)$ is the measured linewidth, $\Gamma(0)$ is the 4.2°K strain broadened linewidth and Γ_{sc} is the linewidth resulting from phonon scattering. A Gaussian extraction $\Gamma_{sc}^2 = \Gamma^2(T) - \Gamma^2(0)$ is shown in the Figure for comparison although the Lorentzian combination law is clearly

Figure 3-12. Gaussian (triangles) and Lorentzian (circles) combination laws used for extraction of the residual 4.2°K linewidth compared with theory (solid line) for the temperature dependence of the KBr U-center local mode linewidth. The Lorentzian extraction is preferred.

preferred. Scaling Gethins' theoretical curve by a factor of 6 results in good agreement between theory and experimental data. Hence the change of the theoretical linewidth from a T^2 dependence to some more rapid temperature dependence is correct. This is indicative of the fact that the exact phonon density of states was used in the calculation. However the magnitude of the theoretical prediction is low by a factor of 6 suggesting that perhaps incorrect anharmonicity was assumed (the KH potential parameter ρ was used in the calculations) or that higher order phonon processes are also important.

D. The U-Center Zeeman Effect in KCl

It has been suggested in the literature that the U-center Faraday rotation should be observable on the basis of a comparison of the expected Verdet constant (in deg/gauss-cm) with that measured for F-centers.²⁷ We have attempted to measure this rotation for KCl U-centers using a 100 kg magnet and have not observed any Faraday rotation. The discrepancy between the predicted ease of measuring this effect and our observations derives from the assumptions used in calculating the expected Faraday rotation from the Verdet constant.

The Hamiltonian of the U-center in a magnetic field is given by

$$\mathcal{H} = \frac{\vec{p}^2}{2m} + \frac{1}{2}m\omega_0^2\vec{q}^2 - \frac{e}{mc}\vec{p} \cdot \vec{A}$$

where the first two terms of this expression correspond to the U-center in a spherically symmetric harmonic potential well. The last term in this Hamiltonian is the perturbation caused by the magnetic field where $\vec{A}$ is the vector potential of the magnetic field. In this Hamiltonian the harmonic lattice phonon terms are ignored as is the anharmonic coupling of the phonons to the U-center which was important in an earlier section in determining the temperature dependence of the local mode linewidth.

For electromagnetic radiation propagating along the z-axis, application of a magnetic field of strength B along the z-direction results in Zeeman splitting of the U-center absorption line into two absorption lines for different circular polarizations. For a 100 kg field this splitting is estimated to be

$$\Delta\omega = \frac{eB}{2\pi mc^2} = 5 \times 10^{-3} \text{ cm}^{-1}$$

which is 3% of the linewidth of the U-center in KCl at 4.2°K. The effective charge of the U-center e^* has been estimated to be 0.8e and the Zeeman effect provides a way of measuring the effective charge.⁷ From measurements in earlier sections on the U-center local mode temperature dependence, this splitting is about equal to the deviation in the 4.2°K measurements. However, to incorporate the 100 kg magnet into the light pipe system, several additional feet of light pipe and an additional right

angle bend are needed. Also, the cooled light pipe used in the temperature dependent studies is not easily adapted to the magnet system. As a consequence of the indicated changes necessary to investigate the Zeeman effect, an order of magnitude in signal would easily be lost compared to the linewidth temperature dependent studies. Hence the Zeeman splitting is expected to be unobservable with our present cryostats in a direct measurement of the change in the local mode linewidth.

The Faraday rotation of the plane of polarization is another manifestation of the Zeeman splitting of the U-center local mode absorption. The absorption constant α is related to the index of refraction n through the Kramers-Kronig relations and variation in α thus results in a change in n . So if the local mode absorption splits into two absorption lines for right and left hand circularly polarized light (as in the Zeeman effect), the index of refraction at a frequency near the absorption will be different for the two circular polarizations. This difference in the index of refraction results in different velocities of propagation for the two circular polarizations and hence a Faraday rotation in the plane of polarization derives from one circular component lagging behind the other.

The maximum Faraday rotation occurs near the center of the unshifted line ω_0 and is given by²⁷

$$\Delta\theta_0 \equiv BVt \approx - \frac{2\pi N e^3 B t}{[\epsilon(\infty)]^{\frac{1}{2}} c^2 (m\Gamma)^2}$$

where $\epsilon(\infty)$ is the high frequency dielectric constant, N is the number of defect centers/cc, t is the crystal thickness, V is the Verdet constant and Γ is in rad/sec. The maximum in the absorption constant which occurs at the local mode frequency is

$$\alpha_0 = \frac{8\pi N e^2}{c^2 (m\Gamma)}$$

For KCl U-centers, Cunningham and Hardy calculated $V = -13.77 \times 10^{-4}$ deg/gauss-cm and $\alpha_0 = 411 \text{ cm}^{-1}$ for $N = 10^{17}$ cc and $\Gamma = 0.15 \text{ cm}^{-1}$. However, for some radiation to be transmitted through the crystal and for the Faraday rotation to be observed, we require that $\alpha_0 t \approx 1$. Hence for $B = 100$ kg, the Faraday rotation is only

$$\Delta\theta_0 = VBt = -0.34^\circ$$

even though the Verdet constant for the U-center and F-center are comparable. The observation of the Faraday rotation for the U-center is further complicated by the need to use a spectrometer resolution comparable to the 0.15 cm^{-1} U-center linewidth in the 500 cm^{-1} region of the infrared. The absolute value of the Verdet constant decreases precipitously as the frequency of the electromagnetic radiation is changed from ω_0 .

We attempted to observe the Faraday rotation in KCl U-center crystals using polarizers made from a plastic film echelette diffraction grating.⁹⁰ Aluminum was evaporated onto the grating surface from an oblique angle in order to coat only a portion of the grooves of the grating. Two of the resulting polarizers transmitted $\mathcal{T}_{\parallel} \approx 50\%$ of the 500 cm^{-1} infrared radiation when grooves of the polarizers were parallel but only $\mathcal{T}_{\perp} \approx 2\%$ when the grooves of the polarizers were perpendicular.

These polarizers were glued to opposite sides of a 1 mm thick KCl U-center crystal for which $\alpha_0 t \approx 1$ as observed with 1 mm spectrometer slits. The polarizers were crossed so that radiation with an unrotated plane of polarization would be highly attenuated. This geometry assisted in filtering background radiation which would otherwise have caused considerable heating of the He^3 detector used in these measurements. Faraday rotation occurring at ω_0 would be expected to result in increased transmission at that frequency. The increase in transmission is given by projecting the rotated plane of polarization onto the second polarizer. Since $\sin(\Delta\theta_0) \approx -0.006$, at most an increase in the signal transmitted of

$$\mathcal{T}_{\parallel} \sin(\Delta\theta_0) / \mathcal{T}_{\perp} = 15\%$$

is expected on application of a 100 kg magnetic field. However the resolution of our measurements was a factor

of 4 lower than that needed just to bracket Γ , and the signal to noise ratio was only 20 even at this resolution, so the Faraday rotation was not observed.

In both the Zeeman effect and the Faraday rotation measurements described above the expected effect was beyond the detection limits of our instrumentation by roughly an order of magnitude in signal to noise. Careful application of techniques minimizing signal losses (e.g. elimination of unneeded vacuum windows) could result in the observation of these magnetic effects.

E. Summary and Conclusions

Two different manifestations of crystalline anharmonicity have been considered in conjunction with the U-center impurity in alkali halides. A direct observation of anharmonic effects involves the use of hydrostatic pressure techniques. The anharmonicity of the potential well of the U-center results in a frequency shift as pressure is applied to the crystal. Measurements were performed on the KBr, KCl and NaCl local mode absorptions. Using the Grüneisen constant γ to characterize the anharmonicity, theoretical predictions of γ were made and compared to the experimental observations for KBr. The concept of a local compressibility is central to these calculations, and the results indicate that the preferred value of the Huggens-Mayer parameter ρ for KBr is $0.365 \text{ \AA}$ which is only 8% larger than the value for the

KBr bulk crystal.

In addition to measuring the hydrostatic pressure shift of the local mode frequency, the pressure dependence of the KBr U-center phonon side bands was observed. In this case information is obtained about the bulk crystal anharmonicity from the side band frequency shifts. About 80 cm^{-1} from the U-center absorption, there is a side band absorption of particular interest since it can be identified with a limited region of the Brillouin zone. For these phonons a measured value of $\gamma = 1.93 \pm 0.1$ is obtained which agrees well with the value of 1.91 predicted from a shell model calculation.

The temperature dependence measurements of the U-center linewidth in KBr, KCl and NaCl constitute another observation of the U-center anharmonicity. The high resolution spectrometer and cold filtered Ge:Cu detector were essential to obtaining the high resolution necessary to accurately determine the low temperature linewidths. In addition the interferometer of Dr. H. Gush provided the resolution required to investigate the possibility of an isotope effect. However no isotope effects were identified in the measurements. Two models of the linewidth each with two adjustable parameters, were compared with the experimental measurements and adequate agreement was obtained for KBr and KCl U-center crystals. Comparison of the KBr U-center linewidth data with a calculation without adjustable parameters led to the

necessity of extracting the residual 4.2°K linewidth which was attributed to impurity induced strain broadening and not to anharmonic processes. The curvature of the temperature dependent linewidth agrees with the theoretical model, however, the calculated linewidth is a factor of 6 too small at all temperatures.

Attempts to measure the Faraday rotation for U-centers in KCl proved to be unsuccessful. Estimates of the expected size of the Zeeman effect or Faraday rotation indicate that these magnetic effects could be observed with existing experimental techniques.

CHAPTER IV

FAR INFRARED ABSORPTION SPECTRA OF POLYAMINO ACIDS

The characterization of the three dimensional structure of proteins and the relation of this conformation to the primary sequence of amino acids along the protein backbone is important to understanding the biological functions of proteins. Because of the complexity of proteins many different techniques are used to investigate their conformations and the conformations of simpler model polyamino acids. X-ray techniques are useful in establishing the structure of polypeptides that can be crystallized. Inferences about the helical content of polypeptides can be made through the use of circular dichroism (CD) or optical rotary dispersion (ORD) techniques or from dielectric constant measurements.⁹¹

The normal modes of vibration of polypeptides are additional indicators of the conformation the polypeptides adopt.⁹² The study of conformationally sensitive normal modes with infrared spectroscopic techniques was initially confined to the near infrared (3000 to 500 cm^{-1}) where normal modes involving covalent bond stretchings occur.^{17,93} For example, the frequencies of the C=O stretch (amide I, $\omega \approx 1650 \text{ cm}^{-1}$) or the N-H deformation (amide II, $\omega \approx 1550$) are observed to shift by $\approx 20 \text{ cm}^{-1}$

depending upon the conformation of the polypeptide.^{17,93-95} In contrast, the normal modes in the far infrared spectral region (2 to 500 cm^{-1}) involve torsional oscillations or cooperative skeletal vibrations.⁹⁶ The modes in the far infrared are obviously sensitive to the conformation of the polypeptide, and since 1966 there has been growing interest in the far infrared absorption of polypeptides.^{18-20,95-97}

A. Description of Polypeptides

The polypeptides whose far infrared properties we measured were principally synthetic homopolymers consisting of identical amino acid monomers covalently bonded together to form long chains. The amino acid monomer is represented by the formula

where R is the side chain which distinguishes between different amino acids. A list of the R groups for the amino acids with which we were mainly concerned is given in Table 4-1. These amino acids vary in complexity from glycine, where the side chain is just a hydrogen atom, to γ -benzyl-L-glutamate (BLG), where it includes a benzene ring. For proline the side chain is folded around with its end carbon bonded to the nitrogen of the amino acid to form a 5-vertex ring. These amino acids are

covalently bonded into long polypeptide chains by the formation of peptide bonds as shown below.

Short chain polypeptides consisting of $n = 2$ to 10 residues are referred to as oligopeptides or simply oligomers.

TABLE 4-1

Side Chains of Principal Amino Acids Studied

Amino Acid	Side Chain
glycine	-H
alanine	-CH ₃
leucine	-CH ₂ CH(CH ₃) ₂
proline	-CH ₂ CH ₂ CH ₂ -
γ-benzyl-L-glutamate	-CH ₂ CH ₂ COOCH ₂ C ₆ H ₅

The long biopolymer that results from the formation of a series of peptide bonds can adopt several different conformations depending upon such conditions as the solvent being used, the pH or the temperature of the solution. These conformations are shown in Figure 4-1.⁹⁸ In the random coil conformation the polymer extends randomly in space with no definite order beyond the primary order of

Alpha Helix

Beta Conformation

Random Chain

Figure 4-1. Conformations of polypeptides (after Reference 98) showing the alpha helix (top), beta conformation (middle) and random chain (bottom).

amino acid residues along the polymer backbone. In the other two conformations there is secondary structure present. The beta conformation results from interchain hydrogen bonding. A two dimensional plane or sheet results with the individual polymer chains extending parallel to one another in one direction in the plane. In the alpha helical conformation the polymer backbone is wound in the form of a helix represented by dashes in the Figure. This structure is stabilized by hydrogen bonds which occur between an amino acid and its third nearest neighbor along the helix. These bonds are represented by dashes along the helical axis.

B. Detection of the Far Infrared Normal Modes of the α -Helix

1. Models of the Normal Vibrations

Our studies of biopolymers were primarily concerned with observing the low frequency far infrared normal modes of vibration of the α -helical conformation. Simplified model calculations of the low frequency vibrational modes have been published for the α -helix which predict conformationally sensitive infrared active modes.^{18,99} The observation of these modes would serve as a check of the models. In addition, the relative absence of absorption in nonpolar organic solvents in the far infrared suggests that these low frequency modes of polymers could be used to monitor conformational

transitions occurring in solution.

The dispersion curves for α -helical poly-L-alanine (PLA) have been calculated by several authors.^{20,23,100} In these normal mode calculations the Wilson GF matrix method is employed.⁹² Typically the alanine methyl group side chain (CH_3) is treated as a single dynamical unit. The spatial arrangement of the 7 atoms composing the amino acid residue repeat unit is taken from x-ray studies of the α -helix and the force constants for the various bonds are obtained from the frequencies of oscillation of small molecules. The calculations treat the α -helix as a perfectly formed rigid rod isolated from interactions with neighboring molecules. The higher frequency modes that result have frequencies of oscillation that are nearly independent of the phase ϕ between nearest neighbor amino acid residues since these modes involve localized oscillations of individual residues. In contrast, the low frequency modes involve cooperative skeletal motion and the frequencies of these modes are extremely phase dependent.

The lowest frequency modes of oscillation can be described by a simplified model which replaces the amino acid residue by a single dynamical unit.^{18,99} This unit is bonded to its nearest and third nearest neighbors and solving the equivalent one dimensional problem results in the relation for the longitudinal acoustic (LA) branch

$$\omega = 2 \left[\omega_1^2 \sin^2 \left(\frac{\varphi}{2} \right) + \omega_3^2 \sin^2 \left(\frac{3\varphi}{2} \right) \right]^{\frac{1}{2}}$$

where ω_3^2 expresses the resistance of the hydrogen bond to compression and ω_1^2 expresses the resistance of the rest of the helical backbone to compression. This dispersion curve is plotted at the right where the unusual dip results from the hydrogen bond not being compressed for a phase difference of 120° between nearest neighbors. If

$(\omega_3/\omega_1)^2 > 3$ a point of inflection occurs instead of a minimum at $\varphi = 120^\circ$.¹⁸

Removing the restriction of motion in one direction results in an optic branch and an additional acoustic branch. Taken together the three dispersion curves comprise a model of the low frequency branches of more complete normal mode calculations which treat the 7 atoms of the amino acid separately. The low frequency structure of these complete calculations for the 3.6 helix is shown in Figure 4-2 where the (20) dispersion curve is the LA branch.

The first infrared active points of the dispersion curves occur at $\varphi = 0$ for infinite length polymers or at $\varphi = \pi/n$ (accordian like motion of the helix for the LA

Figure 4-2. Low frequency dispersion curves (after Reference 99) showing the effect of variation of the hydrogen bond strength on the various branches.

branch) for finite chains of length n . These modes have A type symmetry and are infrared active for electric field vector polarizations parallel to the α -helix. The other infrared active points for a helix with 3.6 amino acid residues per turn of the helix occur at $\varphi = 100^\circ$ and are E_1 modes which are infrared active for electric vector polarization perpendicular to the α -helix. Raman active points occur at $\varphi = 0$, $\varphi = 100^\circ$ and $\varphi = 160^\circ$ (corresponding to A, E_1 and E_2 modes respectively²³).

2. Measurement of the Far Infrared Absorption

We have measured the far infrared transmission spectra of a variety of polypeptides using Fourier transform techniques in an investigation of the low frequency infrared active modes. The transmission spectra were measured under a variety of conditions with polymers in the solid state or in solution. The spectra of samples in the solid state were measured at 4.2°K and/or 300°K . The polypeptide samples were typically received in powdered form. The origin of these samples is given in Table 4-2. Here DP stands for degree of polymerization as determined from the average molecular weight.

The polypeptide powders were mixed with paraffin powder that had been pulverized earlier at liquid nitrogen temperature with a mortar and pestle and then, after being dried in a vacuum for one minute, the mixtures were compressed at a pressure of 200 psi to form pellets. This pressure is a factor of 10 lower than that used in

TABLE 4-2

Sources and Identification of Polypeptides

Polypeptide	Source	Lot No.	DP
PBLG	*	RA 195	160
PBLG	*	RA 215	740
PBLG	*	RA 201	1500
P(BLG + 3% gly)	*	RA 132	700
PHBG	*	-----	76
P(HBG + 3% gly)	*	RA 178 F III	100
PLA	Miles	AL 52	30
PLA	Mann**	U-1242	680
alanine oligomers	Miles	ALAL10, 3AL9, 2 to 6 4AL6, 5AL5 and 6AL6	
poly-L-leucine	Miles	LE 37	Indeterminable
poly-DL-leucine	Miles	LE 35	35
poly-L-proline	Miles	PR 15	120
poly-glycine	Miles	G - 41	Indeterminable
poly-L-lysine hydrobromide	Pilot	L - 90	1000
poly-DL-lysine hydrobromide	Miles	LY 114A	~35 to 120
whale myoglobin	Miles	10	1x crystalline
egg albumin	Miles	18	5x crystalline
amino acid monomers	Miles	---	-----

*Provided by A. Lewis and H. A. Scheraga.

**Provided by R. E. Hughes.

making KBr pellets. A typical pellet has 200 mg of paraffin and 15 mg of polymer. For a unit density polymer distributed uniformly across the $\frac{1}{2}$ " diameter far infrared beam this amount of polymer corresponds to a thickness of 0.012 cm. Paraffin is a suitable matrix for these samples since it is transparent for frequencies below 650 cm^{-1} with the exception of a narrow absorption at 80 cm^{-1} . This absorption is compensated for by using the spectrum of an equal amount of pure paraffin as a divisor. In the press, paper disks were used above and below the paraffin pellet to facilitate separation of the sample from the metal anvils of the press.

The infrared absorption measurements on polymers dissolved in solution are dependent on the solubilities of the various samples.¹⁷ Organic solvents such as carbon tetrachloride, benzene or chloroform are ideal for far infrared studies since they are reasonably transparent.¹⁰¹⁻¹⁰³ Far infrared studies using these solvents can be made easily with concentrations of polymer in the 1 to 5% range and liquid cells with a path length of up to 1 cm. At higher concentrations (~50%) observation of sample absorption is even possible in 0.01 cm thicknesses of water when Fourier transform techniques are used. These measurements on samples dissolved in water were confined to the $\omega < 100\text{ cm}^{-1}$ region because of the increased absorption of water at higher frequencies.^{104,105}

Figures 4-3 and 4-4 show our measurements of the absorption of several different liquids which might be of interest for solution studies. Dichloroacetic acid is polar and the absorption features observed in Figure 4-3 make it unsuitable for solution studies. On the other hand, these and other studies of benzene and chloroform indicate that these solvents could be used easily for absorption studies of polymers in solution.¹⁰¹

C. Poly- γ -benzyl-L-glutamate

Infrared absorption and Raman scattering measurements have been reported in the literature for poly- γ -benzyl-L-glutamate (PBLG) previously.¹⁰⁶⁻¹⁰⁸ Recently the infrared absorption measurements were extended into the far infrared spectral region (to $\omega \geq 50 \text{ cm}^{-1}$).¹⁰⁹ High molecular weight PBLG is known to assume the α -helical conformation in the solid state (see references cited in Reference 107) and the presence of α -helical structure in our samples is confirmed by their far infrared absorption spectra. For a series of polymers absorption lines at $\approx 90 \text{ cm}^{-1}$ and $\approx 120 \text{ cm}^{-1}$ have been identified with the α -helical conformation.¹¹⁰ The far infrared transmission of PLA in the solid state is shown in Figure 4-5 for comparison with the transmission of PBLG shown in the same Figure. The absorption lines of the PBLG are not as well defined as the PLA absorption lines possibly because of steric hindrance of the relatively complex PBLG

Figure 4-3. Absorption spectra of dichloroacetic acid and benzene.

Figure 4-4. Absorption spectra of D_2O , H_2O as a function of temperature, H_2O , benzene and chloroform.

Figure 4-5. Transmission spectra of PLA and PBLG.

side chain.

The transmission of PBLG can be compared with the transmission spectrum of the BLG monomer shown in Figure 4-6. There are on the order of 60 absorption lines in the region shown ($\omega \lesssim 300 \text{ cm}^{-1}$). The sheer number of far infrared absorption lines is at first surprising even for the complex BLG monomer since for n atoms $3n - 3 = 84$ is the maximum number of normal modes expected in the 0 to 3000 cm^{-1} region for an isolated monomer. The large number of observed lines can be understood in terms of lattice modes which complicate the low frequency absorption spectrum.¹⁰⁸ Because of the complexity of both the absorption spectrum and the BLG molecule, we shall not attempt identification of the far infrared absorption in terms of normal mode analysis. It is notable, however, that the lines for the monomer are considerably more abundant and have a much smaller half-width than the absorptions observed in the case of PBLG.

In the spectrum of PBLG no absorption lines are observed at frequencies lower than 90 cm^{-1} where a shoulder occurs in the absorption constant. It is precisely the region around 20 to 50 cm^{-1} where the longitudinal acoustic infrared active modes had been predicted for PLA.^{20,23} Since these low frequency modes are sensitive to the polymer conformation, we searched (to no avail) for these modes in PBLG under a variety of conditions of temperature, polymer length, and polymer composition. Spectra of PBLG

Figure 4-6. Transmission spectrum of γ -benzyl-L-glutamate.

dissolved in chloroform or benzene were also measured to assess the differences between spectra in solution and in the solid state.

The higher frequency far infrared modes which are observed and also are conformationally sensitive were used to monitor the state of the polymer as the various parameters were changed. In fact, part of the difficulty in observing the acoustic modes in the polymer is related to the reason for the lack of precisely defined higher frequency far infrared absorption lines with small half-widths. The breadth of the far infrared absorption features of PBLG shown in Figure 4-5 obscures the normal mode content of the spectrum.

The results of the series of measurements on PBLG under varied conditions are shown in Figures 4-7 and 4-8. In the top two panels of Figure 4-7 the solution spectra of PBLG are shown. Aside from the noise observed on the solution spectra, the absorption features are nearly identical for a 5% concentration of PBLG in chloroform or for a 1% concentration of PBLG in benzene. The observed absorption lines are associated with the α -helix which is the conformation assumed by PBLG in chloroform or benzene.⁹¹

The absorption observed for PBLG in these solutions is remarkably similar to the absorption in the solid state shown in the bottom two panels of Figure 4-7. Analogous results have been obtained in the case of poly-L-proline where near infrared and Raman measurements reveal only

Figure 4-7. Transmission spectra of chloroform + 5% PBLG and benzene + 1% PBLG and of solid PBLG at 300°K and 4.2°K.

Figure 4-8. Transmission spectra of 1500 DP and 740 DP PBLG at 300°K and of P(BLG + 3% gly) at 300°K and 4.2°K.

minor differences between spectra of the polymer in the solid state or dissolved in H_2O .^{17,111,112} The spectra shown here are 4.2°K and 300°K measurements on the same sample. The sample was a PBLG film cast from chloroform. During the process of evaporation of the chloroform when concentrations of 10 to 15% polymer are reached, the PBLG goes through a liquid crystalline transition in which the α -helical polymer chains lie parallel to one another forming planar structures.¹¹³ No orientation of these planes was attempted and the evaporation was not controlled as it might be to maximize the liquid crystalline order. Only a slight improvement in the resolution of features in the PBLG absorption spectrum was observed on cooling the sample to 4.2°K.

The spectra shown in Figure 4-7 all derived from the same preparation of PBLG with DP = 160. Changes in the polymer length and composition were made and the results of far infrared absorption studies of these polymers are shown in Figure 4-8. Measurements on polymers with DP = 1500 and DP = 740 are shown in the top two panels of that Figure. Here the principal difference between these spectra and the solid state PBLG spectra shown earlier for the 160 DP sample is that less sample was used in these spectra so that the absorption is not as strongly emphasized. Otherwise the features of the absorption spectra are almost identical independent of polymer length.

The final PBLG transmission spectra are shown in the bottom half of Figure 4-8. The composition of the PBLG was varied in this case by incorporating 3% glycine into the polymer to form a random copolymer (although there might be some grouping of the glycine). The infrared ($\omega > 200 \text{ cm}^{-1}$) and Raman ($\omega > 30 \text{ cm}^{-1}$) spectra of other copolymers have been reported elsewhere.^{26,114,115} These measurements indicate that glycine destabilizes the α -helix causing the copolymer to adopt the beta or random coil conformations at high glycine concentrations. Consequently we would expect some broadening of the pure PBLG absorption lines to occur in the case of P(BLG + 3% gly) and a slight broadening and lessening of the intensity of the absorption bands is observed in Figure 4-8. Perhaps the most notable change that occurs is the virtual disappearance of the absorption line at 225 cm^{-1} in the 4.2°K spectrum of PBLG. Also there is no significant improvement in the definition of the absorption bands on cooling the copolymer from 300°K to 4.2°K .

The similarity of the various absorption spectra of PBLG reported here suggests that the conformation of the polymers is similar in solution or the solid state independent of chain length. The marked resemblance of the solid state and solution spectra implies that crystalline order cannot be important in determining the far infrared absorption. This result is consistent with the assignment of far infrared absorption lines to internal

motions of the α -helix. Removal of $k_B T$ fluctuations by cooling the solid PBLG samples to 4.2°K only results in slightly improved definition of the absorption features. Evidently the P(BLG + 3% gly) copolymer is already sufficiently disordered so that removal of thermally induced disorder ($k_B T$ fluctuations) has no effect on the broad absorption features observed.

D. Glycine, Alanine, Leucine and Proline

The far infrared absorption of various amino acid monomers provides some contrast to the measurements on PBLG and the other polymers. Measurements of absorption spectra extending into the far infrared spectral region have been made previously for several amino acids at liquid nitrogen temperatures, however measurements at 4.2°K are relatively rare.¹¹⁶⁻¹¹⁸ Since $100^\circ\text{K} = 70\text{ cm}^{-1}$, thermal energies at liquid nitrogen temperature are about the same order of magnitude as the far infrared energies under consideration and further cooling would be expected to improve the definition of the low frequency far infrared spectra.

The results of our measurements on glycine, alanine, leucine and proline are shown in Figure 4-9. Sidestepping the question of the interpretation of the individual lines in the complex absorption spectra, we undertake instead a comparison of the general features with those observed in the PBLG spectra. Cooling the samples results in the

Figure 4-9. Transmission spectra of glycine, alanine, leucine and proline in the solid state at 4.2°K and of proline in H₂O at 300°K and 4.2°K.

appearance of a series of narrow absorption lines which are considerably broadened at higher temperatures. This observation contrasts with the case of PBLG in which only slight improvement in the spectrum is observed on cooling.

The narrow half-widths of the monomer absorptions can be attributed to crystalline lattice modes. The low frequency far infrared absorption lines are not present when an amino acid is dissolved in water. The bottom two panels in Figure 4-9 show the results of far infrared absorption studies of proline dissolved in H_2O . For the $300^\circ K$ measurements pure H_2O was used as a divisor spectrum, while for the $4.2^\circ K$ measurements a blank sample position was used as the divisor. Consequently the H_2O absorption which increases with frequency is observed in the low temperature spectrum. Roughly the same amount of proline was present in solution (at a concentration of 50%) as was in the solid proline sample. However none of the absorption lines of the solid proline sample can be identified in the spectra of proline in solution, although a broad absorption band is observed at $300^\circ K$ in the solution spectrum. The disorder of the $300^\circ K$ solution spectrum is frozen in on cooling to $4.2^\circ K$ and no modes associated with a well defined lattice are observed.

In the light of these measurements on amino acid monomers the lack of appreciable temperature dependence in the PBLG spectra is not surprising. It is well known

that good x-ray data are difficult to obtain on the poly-amino acids because of difficulties in obtaining well defined crystals.¹¹⁹ Consequently the spectra observed for PBLG in solution or in the solid state are expected to be similar.

E. Poly-L-proline, Poly-L-leucine and Poly-DL-leucine

In the case of the polymers considered thus far in this chapter no low frequency absorption has been observed that could be identified with the predicted infrared active longitudinal acoustic modes. In the case of poly-L-proline, poly-L-leucine and poly-DL-leucine, a broad low frequency absorption line is observed at 65 cm^{-1} which might tentatively be identified as arising from the LA branch. Polarization studies are necessary to establish the symmetry of the observed absorption and to assist in the assignment of the mode. However because of solubility problems, these polarization measurements were not performed. The poly-DL-leucine was soluble in carbon tetrachloride and the poly-L-proline was soluble in acetic acid but both of these polymers were too short to expect appreciable orientation to be possible. On the other hand the poly-L-leucine was insoluble in all the common solvents tried.¹⁷

Figure 4-10 shows the transmission spectrum of poly-L-proline. The poly-L-proline is in form I (right handed helix) as verified by comparison of the far infrared

Figure 4-10. Transmission spectrum of poly-L-proline.

absorption with other published data in the $\omega \geq 80 \text{ cm}^{-1}$ region.¹²⁰ Far infrared and Raman measurements have been performed on the proline oligomers as well as on the polymer in forms I and II^{108,120,121} and normal mode calculations have been completed on poly-L-proline I for comparison with the observed modes.¹²² The calculations predict an A mode at 75 cm^{-1} and an E_1 mode (LA) at 43 cm^{-1} . However, since the skeletal force constants are adjusted to fit the higher frequency modes that were observed previously, the 65 cm^{-1} absorption could result from either of these predicted modes and polarization studies are necessary to establish its symmetry. Comparable calculations by Itoh and Shimanouchi for PLA place the A mode at 80 cm^{-1} and the E_1 mode at 44 cm^{-1} .²⁰

The right handed helix of poly-L-proline I is somewhat unusual since it is not stabilized by hydrogen bonds. One amino group hydrogen is replaced by bonding of the amino nitrogen to the end of the side chain of the amino acid.⁹¹ The five member ring that results from this bond formation is an important part of the backbone structure. In spite of this difference from the standard α -helix stabilized by hydrogen bonds, the resulting right handed helix of poly-L-proline I is not all that different with a translation and rotation per residue of $1.90 \text{ \AA}$ and 108° respectively instead of the standard α -helical $1.50 \text{ \AA}$ and 100° .⁹¹

Figure 4-11 shows the far infrared transmission spectra of poly-L-leucine and poly-DL-leucine. Again, higher frequency far infrared measurements ($\omega \geq 80 \text{ cm}^{-1}$) have been performed previously on poly-L-leucine as have Raman scattering measurements.^{107,108,110} The similarity of the low frequency far infrared absorption of these polymers and poly-L-proline I is at first surprising since the poly-L-proline does not contain hydrogen bonds. However, recall that at the infrared active points on the dispersion curves shown in Figure 4-2 ($\phi = 0^\circ$ and $\phi = 100^\circ$) the hydrogen bond strength does not affect the frequency, as indicated by the different curves shown in the Figure for several hydrogen bond strengths. Furthermore because of the difference in the side chains of proline and leucine and the manner in which the proline side chain is incorporated into the backbone of the polymer, we do not expect the observed 65 cm^{-1} bands to be related to isolated side chain torsions.

Finally the modes are not related to the crystal structure since, as mentioned earlier in the case of PBLG, no precisely defined lattice is present in these polymers. This is confirmed by our powder x-ray diffraction measurements on PBLG, poly-L-leucine and poly-L-proline shown in Figure 4-12 (the other substances whose x-ray diffraction patterns are shown are discussed in Appendix B) and by other x-ray measurements.^{91,115,119} In Figure 4-12 the triangles shown indicate the height

Figure 4-11. Transmission spectra of poly-L-leucine and poly-DL-leucine.

Figure 4-12. Powder x-ray diffraction data for polyox, PBLG, poly-L-leucine, poly-L-proline, sodium oleate and stearic acid.

and width of the x-ray diffraction peaks observed. A Cu source was used for these measurements with $\lambda = 1.54 \text{ \AA}$. The large x-ray peak width of the homopolymers is indicative of the lack of precisely defined crystal structure for these samples.

In Figure 4-11 the spectral features shown for poly-DL-leucine have a greater half-width than those shown for poly-L-leucine. The difference between the L- and D-amino acids is in the tetrahedral steric arrangement of the atoms as shown below.

L-amino acid

D-amino acid

The L-amino acids preferentially form a right handed helix while for the D-amino acids the left handed helix is more stable. The incorporation of L- and D-amino acids in the same polymer in a ratio of 1:1, as is the case for the poly-DL-leucine studied here, is expected to perturb the α -helix.

Copolymers of D- and L-amino acids have been observed to contain destabilized helices in solution studies using optical rotary dispersion techniques.⁹¹ However, near infrared studies indicated the presence of appreciable helical content in stereoisomer copolymers of γ -methylglutamate and γ -benzylglutamate.⁹⁵ This result is

supported by recent neutron scattering measurements on poly-DL-alanine at energies characteristic of the far infrared spectral region. In these measurements a decrease in the scattering amplitude was observed but the features in the poly-L-alanine and poly-DL-alanine scattering spectra were similar.¹²³ In the case of stereoisomer copolymers of leucine, near infrared absorption studies have also indicated the presence of considerable helical content.¹²⁴ The effect of proceeding from the pure L to the 1:1 stereoisomer composition has been explained in terms of progression from regular α -helix to perturbed α -helix with disordered parts.^{95,125} A decrease in the absorption strengths of the α -helical bands and an increase in the far infrared linewidths might be expected from the disorder induced by the incorporation of L- and D-stereoisomers in the same helix. This expectation is indeed confirmed by the data shown in Figure 4-11.

The difference in definition of the poly-L-leucine and poly-DL-leucine spectra is attributed to the helix destabilizing effect of the stereoisomers in the poly-DL-leucine and not to differences in the polymer lengths. In infrared absorption studies around 600 cm^{-1} , the definition of spectra of poly- γ -benzyl-DL-glutamate was only slightly affected by increasing the copolymer length from 41 to 151 residues. In addition the far infrared spectra of poly-L-alanine to be reported in the next

section showed no appreciable change in the linewidths on increasing the polymer length from 30 to 680 residues. The 65 cm^{-1} far infrared absorption line tentatively identified with the LA branch is observed in the absorption of both poly-L-leucine and poly-DL-leucine.

The difference in the far infrared spectra of poly-L-leucine and poly-DL-leucine is larger than any change observed during the variation of a series of parameters reported earlier in the case of PBLG. However, even the absorption lines of poly-L-leucine have a larger half-width than observed in the case of the amino acid monomers.

F. Alanine Oligomers and Poly-L-alanine

As an extension of our far infrared measurements on polymers and their monomers, we have investigated the far infrared absorption of a series of alanine oligomers ($n = 2$ to 6) and of poly-L-alanine ($DP = 30$ and 680). During these studies we have also searched for the low frequency longitudinal acoustic modes of the polymer. For PLA α -helices containing n amino acid residues, the frequency of the $\phi = \pi/n$ infrared active LA accordian-like mode is inversely proportional to n and is predicted to be in the 15 to 30 cm^{-1} range for $n = 30$ and less than 1 cm^{-1} for $n = 680$. On the other hand the $\phi = 100^\circ$ infrared active mode is nearly independent of n and is expected to lie in the 25 to 45 cm^{-1} range.^{20,23}

Infrared absorption and Raman scattering measurements

have been performed previously on α -helical homopolymers of alanine and compared to model calculations of the expected excitation frequencies.¹⁹⁻²³ Because of the difficulty of measuring absorption spectra at far infrared frequencies, the infrared measurements have not extended below $\sim 80 \text{ cm}^{-1}$. Infrared absorption measurements on the alanine oligomers have been performed for frequencies greater than 200 cm^{-1} ^{126,127} and Raman scattering measurements have also been performed on these oligomers.^{108,128}

1. Comparison of Alanine Oligomer and PLA Absorption Spectra

We have measured the far infrared absorption of the alanine oligomers and PLA for frequencies greater than 4 cm^{-1} . The results of our measurements on these samples at 4.2°K for frequencies between 4 and 90 cm^{-1} are shown in Figure 4-13. In the lower frequency region shown in the Figure, three times as much polymer was used to enhance the absorption. It is observed that the shorter oligomers have many low frequency far infrared absorptions lines with comparatively small half-widths. The lowest frequency absorption line observed in the tetramer, pentamer and hexamer broadens and shifts to lower frequencies in the progression toward longer oligomer chains. Indeed, aside from the low frequency band at 30 cm^{-1} in the hexamer absorption spectrum, no other absorption lines are observed in the region below 90 cm^{-1} for the hexamer.

Figure 4-13. Transmission spectra (4 to 90 cm^{-1}) of PLA and the L-alanine oligomers ($n = 2$ to 6) at 4.2°K.

Figure 4-14 shows the transmission at 300°K of the alanine oligomers and PLA from 30 to 90 cm^{-1} . It is noted that the comparatively sharp absorption lines of the shorter oligomers are more affected by the temperature change than are the absorption lines of the longer oligomers. Similar results are observed in the higher frequency region. Figure 4-15 shows the spectra of the alanine samples at 4.2°K for frequencies up to 320 cm^{-1} and Figure 4-16 shows comparable spectra at 300°K. The room temperature spectra of the oligomers and polymers all exhibit similar linewidths. However for the polymer and hexamer spectra, relatively slight improvement in definition is achieved on cooling to 4.2°K while the change in the spectra of the shorter oligomers at 4.2°K is striking.

The narrow linewidths and the temperature dependence of the shorter oligomer 4.2°K far infrared spectra are consistent with earlier interpretations of the difference between polymer and amino acid low temperature spectra in the solid state. The longer oligomers are expected to be more difficult to crystallize than the shorter oligomers.¹¹⁹ In fact, of the oligomers shown only di-L-alanine has had its crystal structure determined by x-ray diffraction techniques.¹²⁹ Figure 4-17 shows a schematic diagram of our powder x-ray diffraction measurements for the alanine oligomers and PLA. There are more peaks observed and the peak widths are narrower for the shorter oligomers suggesting that these oligomers have a

Figure 4-14. Transmission spectra (30 to 90 cm^{-1}) of PLA and the L-alanine oligomers ($n = 2$ to 6) at 300°K.

Figure 4-15. Transmission spectra (40 to 320 cm⁻¹) of PLA and the L-alanine oligomers (n = 2 to 6) at 4.2°K.

Figure 4-16. Transmission spectra (40 to 320 cm⁻¹) of PLA and the L-alanine oligomers (n = 2 to 6) at 300°K.

Figure 4-17. Powder x-ray diffraction data for PLA and L-alanine oligomers ($n = 2$ to 6).

better defined crystal structure or a larger effective crystallite size. In contrast thermal disorder is frozen into the polymer and longer oligomers in the solid state so cooling them does not result in much narrowing of the far infrared absorption lines.

The broad x-ray peaks observed in the diffraction measurements on PLA can be identified with the α - and β -conformations.¹³⁰ The peak at $2\theta = 11.6^\circ$ ($d = 7.7 \text{ \AA}$) results from the α -helical conformation while the peak at $2\theta = 16.6^\circ$ ($d = 5.33 \text{ \AA}$) derives from the presence of some β -conformation in the polymer. Only the hexamer has a peak that coincides with the α or β peaks of the polymer. The position of the lowest angle diffraction peak of the hexamer suggests that it is in the β -conformation. Penta and tetra-L-alanine have diffraction peaks which nearly coincide with those of hexa-L-alanine, again suggesting some similarity in their conformations.

Knowledge of the conformation adopted by oligomers is important in determining the critical length for helix formation and the polymer length needed for β -conformation to be formed. Besides spectroscopic studies a number of investigators have used ORD or CD techniques to assess the conformation of oligomers in solution. In the case of oligomers of BLG it has been estimated that 7 residues or roughly two turns of the helix are necessary for helix formation.^{125,131} Of course the number of residues required for the onset of helicity is dependent

upon the solvent used. In the case of L-alanine oligomers, helix formation is inhibited by strong acids such as trifluoroacetic and dichloroacetic acid.¹³² Trifluoroethanol, on the other hand, favors helix formation and the onset of helicity for L-alanine residues evidently occurs at six residues in this solution.^{132,133}

The infrared and Raman spectroscopic studies of the L-alanine oligomers have indicated that in the solid state these compounds do not assume the α -helical form for $n = 2$ to 6.^{126,128} In particular, the Raman studies suggest that the $n = 3$ to 6 oligomers assume the β -conformation. In the far infrared a variety of absorption lines exist which are conformationally sensitive.^{19,110} In the PLA transmission spectrum shown in Figure 4-18 the 250 and 440 cm^{-1} absorption lines are indicative of the β -conformation (as is a broad absorption centered at 120 cm^{-1}), while the 90 cm^{-1} absorption edge and the 120 and 370 cm^{-1} absorption lines are indicative of the α -helical conformation. In Figures 4-19 and 4-20 transmission spectra of 30 DP PLA with some β content and 680 DP PLA with virtually no β content are shown. In these Figures tri-L-alanine and hexa-L-alanine spectra are shown for comparison. In Figure 4-19 the band at 250 cm^{-1} , attributed to the β form of the polymer, is present in the hexamer spectrum. In addition, there are low frequency absorption lines at 90 and 120 cm^{-1} which correspond to bands of the α -helix. The β -conformation also

Figure 4-18. Transmission spectra (80 to 640 cm⁻¹) of PLA and the L-alanine oligomers (n = 2 to 6) at 4.2°K.

Figure 4-19. Transmission spectra of PLA (DP = 30) and hexa-L-alanine.

Figure 4-20. Transmission spectra of PLA (DP = 680) and tri-L-alanine.

has a broad absorption line at 120 cm^{-1} , however, so it is necessary to consider the higher frequency region shown in Figure 4-18. Here the 440 cm^{-1} β -conformation absorption line is observed in the hexamer spectrum but the 370 cm^{-1} α -conformation line is not observed in agreement with earlier spectroscopic results that the hexamer adopts the β -conformation in the solid state.

Furthermore our results are consistent with the interpretation that the $n = 3$ to 5 alanine oligomers also are in the β -conformation. As shown in Figure 4-18, the far infrared spectra for the trimer through the pentamer contain absorption lines at the 250 cm^{-1} and 440 cm^{-1} frequencies attributed to the β -conformation of the polymer. However the large number of lines observed at 4.2°K resulting from a semblance of crystalline order complicates the conformational assignment. For example, the tri-L-alanine far infrared transmission is shown in expanded form in Figure 4-20. The series of absorption lines at 4.2°K near 250 cm^{-1} merge into a broad absorption band at 300°K . Since for room temperature measurements the effects of crystalline order (such as splitting of absorption lines) are not as apparent as at 4.2°K , the 300°K measurements are in a sense better suited to conformational assignments related to polymers that are not highly crystalline.

2. Low Frequency Far Infrared Absorption of PLA

Now we return to the problem of measuring the low

frequency far infrared absorption of the α -helical modes which are predicted to be infrared active.^{20,23} Recall that the 30 DP PLA was predicted to have one infrared active mode in the 15 to 30 cm^{-1} region and another in the 25 to 45 cm^{-1} region. The 680 DP PLA sample was predicted to have one infrared active mode at less than 1 cm^{-1} and another in the 25 to 45 cm^{-1} region.

Figure 4-21 shows a log-log plot of the absorption constant between 4 and 200 cm^{-1} for the DP = 30 PLA sample at 4.2°K. The resolution used in these measurements was 0.8 cm^{-1} . Since the absorption is weaker at lower frequencies in the Figure, a polymer sample ten times thicker than the samples studied at higher frequencies was used to enhance the absorption. To achieve very thick polymer samples without using too much polymer, the far infrared beam diameter was condensed by a light cone from $\frac{1}{2}$ " to $\frac{3}{32}$ ". The radiation then traversed a section of $\frac{3}{32}$ " diameter light pipe containing the polymer and the beam diameter was subsequently expanded to $\frac{1}{2}$ " by another light cone.

Using thicker samples, however, did not reveal any absorption peaks that could be identified with the predicted LA modes. As shown in Figure 4-21 the absorption constant obeys a power law relation as a function of frequency between 4 and 80 cm^{-1} . At 80 cm^{-1} a higher frequency absorption line results in deviation from the power law and at 4 cm^{-1} deviation from the power law

Figure 4-21. Absorption coefficient of PLA (DP = 30) from 4 to 200 cm^{-1} at 4.2°K.

results from a larger percentage error in the absolute value of the absorption constant than at higher frequencies. Conceivably part of the monotonically increasing absorption may be attributed to some residual solvent molecules adsorbed on the polymer before it was embedded in paraffin.

Transmission spectra with a similar absence of low frequency features were obtained for the 30 DP sample at 300°K (see Figure 4-14) and for the 680 DP sample (see Figure 4-22). Again thicker samples were used in the low frequency region in an attempt to enhance the absorption. Our failure to observe the predicted LA modes is consistent with Raman data below 80 cm⁻¹ obtained using an iodine filter to reduce the Rayleigh background.¹³⁴ These measurements also failed to establish the existence of the low frequency modes. More recently, Raman data obtained using a narrow band interference filter have indicated the presence of a low frequency mode around 50 cm⁻¹ in PLA although Rayleigh scattering complicates the measurement of these low frequency Raman spectra.¹⁰⁸

There are several possible explanations for the lack of low frequency structure in the far infrared absorption measurements. The frequency of the $\varphi = \pi/n$ LA mode is dependent on the polymer length and might be broadened by a distribution of polymer lengths or by random uncoiling of the ends of the PLA α -helix. However the absence

Figure 4-22. Transmission spectra of PHBG at 300°K and of P(HBG + 3% gly) and PLA (DP = 680) at 300°K and 4.2°K .

of the $\varphi = 100^\circ$ LA mode is more difficult to explain. This mode is expected to be infrared active independent of polymer length. Samples up to 2 mm thick (assuming unit density) have produced no absorption lines, and it would seem fortuitous indeed for this mode to be associated with an extremely weak dipole moment.

The absence of the low frequency LA mode in infrared spectra of PLA is related to the breadth of the far infrared modes that are observed at higher frequencies in PLA and the other polymers. These polymers lack the high degree of crystalline order that is important to the observation of low frequency modes. The absence of a well defined crystal structure necessitates consideration of random interactions between individual polymer chains which were neglected in previous model calculations for PLA. In these calculations the PLA molecule was treated as a perfectly formed, isolated entity. Some work has been done on the consequences of arranging polymers in solids or of including defects in the polymers.^{96,135,136} These studies have been concerned primarily with simple model polymers, such as polyethylene, although some of the results are applicable to the biopolymers investigated here. The force constant representing the intermolecular interaction between neighboring atoms of different polymer chains is ≈ 0.02 mdyne/ $\text{\AA}$ which is of the same order of magnitude as some of the weaker force constants used in the single chain model

calculations for PLA.⁹⁶ A random interaction of this size, resulting from lack of a well defined crystal structure, is roughly equivalent to disorder in the intramolecular force constants of the isolated α -helix model.

Another characterization of the interchain interaction strength involves specific heat measurements on PLA.¹³⁷ In the specific heat measurements on the PLA α -helix, one dimensional and three dimensional Debye temperatures were extracted from the temperature dependence of the data. The resultant three dimensional Debye frequency is found to be 35 cm^{-1} . Coupling to random interchain interactions corresponding to this frequency is expected to shift and broaden the predicted low frequency far infrared modes. For example, consider a distribution of force constants $0 < K < K'$ which couple to a mode of force constant K_0 such that the resultant frequency shift $\Delta\omega$ is given by

$$\Delta\omega \propto (\sqrt{K_0 + K} - \sqrt{K_0})$$

The low frequency modes with $K_0 \approx K'$ are affected more than higher frequency modes by this random frequency shift and the associated broadening of the mode.

Finally, it is perhaps surprising that the far infrared linewidths associated with the α -helix are not narrower for the 680 DP PLA than for the 30 DP PLA. It might be expected that the α -helix in the longer polymer would be better ordered and without end effects of the

shorter polymer. However the far infrared linewidths and the absorption strengths of these lines are similar for comparable sample weights of the short or long polymer. Furthermore attempted orientation by us of the PLA did not affect the far infrared spectra appreciably nor was the far infrared absorption of samples oriented by Itoh and Shimanouchi appreciably different from our results.²⁰

The lack of distinction of these spectra from one another probably results from the formation of interrupted helices in the longer PLA sample. Theoretical calculations of the conformation of PLA in H₂O have shown that chains consisting of 54 residues find it energetically favorable to form hairpin bends and the resulting helical segments are 24 residues long.¹³⁸ Of course this calculation depends on the hydrophobic interaction of the alanine and H₂O. Other experimental studies using ORD, viscosity and sedimentation techniques have shown PLA to exist as interrupted helices in DCA.¹³⁹ A recent x-ray scattering measurement has found PLA to exist in DCA in a compact and rigid structure related to the α -helical conformation.¹⁴⁰ The persistence length of the rigid sections of polymer was found to be 44 Å which is a measure of the flexibility of the chain. This persistence length corresponds to an α -helical segment 29 residues long which is conveniently the length of our shorter chain PLA sample.

Although these studies were conducted in solution, similar results are expected in the solid state.¹⁴⁰ As an extension of our comments on the disorder of the PLA samples and the subsequent broadening of the far infrared absorption spectra, measurements on spherulites of PLA might prove interesting.

Spherulites are planar mats formed by the α -helix folding back upon itself as

shown at the right and are

stabilized by the Van der

Waals interaction between adjacent strands of α -helix.¹⁴¹

The 4.2°K far infrared absorption spectrum of these spherulites might include lattice modes or improved definition of the PLA α -helix absorption lines resulting from the regular structure of the spherulites.

G. Far Infrared Absorption of Miscellaneous Polypeptides

1. Poly(hydroxybutylglutamine-co-glycine)

The top three panels of Figure 4-22 show the far infrared transmission spectra of poly(hydroxybutylglutamine) (PHBG) and P(HBG + 3% gly). Raman measurements on these samples have indicated the existence of an abundance of modes in the 30 to 120 cm^{-1} region.²⁶ Some of these modes are expected to have infrared active counterparts, however our far infrared spectra show no absorption lines which can be identified with the Raman modes.

While Raman spectra are unaffected by the large dipole moment of H_2O , part of the absorption observed in the far infrared spectra may result from H_2O adsorbed on the water soluble PHBG samples.¹⁴² However, comparable weights of PLA, PBLG, poly-L-leucine and poly-L-proline, which are not water soluble, produced absorption strengths similar to that observed for PHBG in Figure 4-22.

There are several possible ways that adsorbed water in the biopolymer samples might affect the far infrared absorption spectra. One possible effect merely would be the superposition of the H_2O and polymer absorptions. However sufficient PHBG was used in our measurements to expect to observe the polymer absorption bands easily even if they were masked in this fashion. A second possibility is that the inclusion of water somehow disorders the polymer. This conclusion would contradict the observation of Raman spectra attributed to the α -helical conformation. ORD and CD studies confirm that the PHBG samples adopt the α -helical conformation in H_2O .^{26,143} A third possible explanation is that the dipole moments of the polymer are coupled to bound water molecules. Such coupling of the dipole moments would be expected to broaden the infrared active transitions. Coupling of the quadrupole moments of the polymer and an adsorbed solvent is expected to be a higher order effect and hence the Raman spectra should be less influenced by adsorbed molecules.

Although the last explanation involving adsorbed solvent molecules appears the most attractive of the three, even this interpretation faces serious difficulties. The PHBG samples were first lyophilized and then stored in a desiccator. The PHBG sample was taken from the desiccator and placed directly in the far infrared beam just before the data taking began. On the other hand, the lyophilized P(HBG + 3% gly) sample was taken from the desiccator, weighed, mixed with paraffin, dried in a vacuum for one minute and then pressed into a pellet. The paraffin subsequently should have protected the sample from H₂O adsorption. Hence, although the PHBG samples are water soluble, there does not appear to have been sufficient exposure to air to result in significant adsorption of H₂O molecules. Further precautions that might be taken include forming a polymer + KBr pellet after a longer period of drying under vacuum.

Having discussed the low frequency infrared and Raman data in general, a specific point of disagreement between the two sets of measurements involves the local mode. This mode is observed in the Raman measurements as a weak 61 cm⁻¹ band with a half-width of 1.2 cm⁻¹ and would be better characterized as a gap or resonant mode since it exists between a series of skeletal modes of the polymer observed in the Raman measurements. No comparable narrow absorption is observed in the far infrared spectra. This discrepancy might be explained if the

symmetry of the 61 cm^{-1} mode causes it to be infrared inactive. However the width of this band is surprising. The U-center local mode is one of the narrowest impurity mode absorptions occurring in alkali halides (see Chapter III) and it has a half-width of $\Gamma = 50\text{ cm}^{-1}$ at 300°K . Allowing for the fact that the frequency ω_0 of the U-center local mode is $\approx 500\text{ cm}^{-1}$ and assuming a constant Q for local modes, $Q = \omega_0/\Gamma = 10$ still results in an estimated half-width of 6 cm^{-1} for a 61 cm^{-1} mode at 300°K . Indeed the most narrow low frequency far infrared absorptions we have observed at 300°K in polyamino acids are 5 to 10 cm^{-1} wide (see Figure 4-16). This width is also characteristic of other bands observed in Raman scattering measurements in the low frequency region at 300°K .^{26,108}

Our measurements on PHBG have failed to reveal the expected far infrared absorption bands. In addition to the possible complication of water adsorbed on the polymers, earlier comments about the lack of crystalline order and the attendant effect of broadening the linewidths are applicable to these lyophilized polymers. The broadening of far infrared modes results from polymer disorder which would also be expected to affect the linewidths of the Raman data. As mentioned earlier with respect to PLA, Raman scattering measurements in the low frequency region are complicated by the large Rayleigh background and by grating ghosts and emission lines of the exciting laser.

2. Poly-L-lysine Hydrobromide and Poly-DL-lysine Hydrobromide

The far infrared transmission spectra of poly-L-lysine hydrobromide and poly-DL-lysine hydrobromide are shown in Figure 4-23. These polymers are water soluble so that remarks made in conjunction with PHBG are applicable here as well. Although precautions were taken to exclude water from the samples, part of the observed absorption could possibly be attributed to adsorbed H_2O . No near infrared data was taken on these polymers to assess the conformation of the samples.

3. Poly-glycine

The far infrared transmission spectrum of poly-glycine is shown in Figure 4-23 at 4.2°K. Poly-glycine is hydrophobic and can adopt a β -conformation (form I) or a helical conformation (form II). There have been numerous spectroscopic studies and normal mode calculations for these forms of poly-glycine.^{126,127,144} The far infrared absorption lines in our data at 140, 220 and 270 cm^{-1} can be identified with form I while the 220 and the 270 cm^{-1} lines also are identified with form II. Hence both forms of poly-glycine could be present in our sample.

The far infrared spectrum of polyox shown in Figure 4-23 will be discussed in Appendix B.

4. Myoglobin, Caesin and Egg Albumin

The bottom three panels of Figure 4-24 show our far

Figure 4-23. Transmission spectra of poly-L-lysine hydrobromide, poly-DL-lysine hydrobromide, poly-glycine and polyox.

Figure 4-24. Transmission spectra of ADP, polyadenylic acid, potato starch, whale myoglobin, caesin and egg albumin.

infrared transmission spectra of myoglobin, caesin and egg albumin. Only a broad, rather featureless absorption is apparent for these proteins even after expansion of the transmission scale to emphasize any absorption features in the 200 cm^{-1} region. These results are consistent with other measurements on Mb and other proteins in the 40 to 400 cm^{-1} region.¹⁰⁹ The broad absorption in that region was attributed to lack of long range periodicity within the proteins resulting from (1) the short extension of any one conformation, (2) the differences in amino acid side chains along the protein backbone and (3) nonperiodic intramolecular interactions. Tightly bound water was suggested as another possible cause contributing to the broad absorption. Twenty to 40% of the weight of a protein can be associated with bound water so that care was taken to dry the samples for our far infrared studies (see remarks on PHBG).¹⁴²

A recent article has reported the observation of a series of weak far infrared absorption lines in myoglobin.¹⁴⁵ Changes in the far infrared absorption spectra were induced by denaturing the myoglobin. We have not observed comparable lines in the absorption spectrum of thicker samples of whale myoglobin than those reported. Figure 4-25 shows our data with the transmission scale expanded. This lack of absorption lines is consistent with the earlier measurements.¹⁰⁹

Figure 4-25. Transmission spectrum of whale myoglobin.

The far infrared transmission data shown in the top three panels of Figure 4-24 will be discussed in Appendix B.

H. Summary and Conclusions

In conclusion, we have investigated the far infrared properties of a variety of polyamino acids. The far infrared region previously has proven to be useful for providing information about the conformation of biopolymers since cooperative skeletal motions of the polymers occur in the far infrared.¹¹⁰ However because of the difficulty of measuring spectra in the low frequency region of the far infrared, few measurements have been attempted at frequencies less than 80 cm^{-1} although conformationally sensitive modes have been predicted by normal coordinate analysis to lie in this region.

The most distinctive far infrared spectra have been observed for short chains of amino acids. The amino acids themselves exhibit far infrared spectra with striking temperature dependence. The observation of numerous absorption lines with comparatively small half-widths at 4.2°K is attributed to the presence of crystal structure in the monomer samples. Short chain oligomers of the amino acids possess similar far infrared absorption spectra with a profusion of modes. However in the progression toward longer oligomers, the crystal structure is less precisely defined because of the difficulty of forming crystals from these long molecules. Hence by the

hexamer in the series of alanine oligomers studied, only a few far infrared absorption lines are observed with little temperature dependence. The absorption lines of the hexa-L-alanine are attributed to the presence of β -conformation in the sample and the absorption lines of the trimer through the pentamer are not inconsistent with the interpretation that these samples are also in the β -conformation.¹²⁸

For PLA polymers composed of 30 amino acid residues the far infrared spectra indicate the presence of considerable α -helical conformation as well as β -conformation. No low frequency far infrared absorption lines have been observed for PLA or PBLG, so the far infrared absorption lines studied for these polymers were at frequencies greater than 80 cm^{-1} . These polymers and others investigated have fewer and broader absorption lines than observed in the short alanine oligomer spectra at 4.2°K . Also, as with the hexamer, the far infrared lines have little temperature dependence indicative of poorly defined crystal structure relative to the short oligomers. In a sense this imprecise crystal structure is a mixed blessing. Although narrow far infrared lattice related modes which could be useful in conformational determinations are not observed, the modes that are observed are related to internal motions of the helix as indicated by solution studies on PBLG. The far infrared absorptions observed for PBLG were the same in solution or in the

solid state and are uncomplicated by the presence of lattice related modes as in the case of tri-L-alanine.

The far infrared absorption of several polymers were investigated as different conditions were varied. In order of increasing effect on the far infrared line-width of PBLG the parameters varied include the polymer length, the solid state or solution environment of the polymer, the temperature of the sample and the amino acid impurity content of the polymer. The lack of appreciable change in the far infrared spectra again was taken to be indicative of the absence of high crystalline content in the polymers. Related to this interpretation is the observation that biopolymers form interrupted helices making it difficult to form highly ordered samples.^{139,140} Perhaps the most noticeable change in the far infrared spectra involved comparison of far infrared data for poly-L-leucine and poly-DL-leucine. The difference in the spectra was explained in terms of the L(D)-stereoisomer's preference for forming a right (left) handed helix. Strong far infrared absorption lines associated with the helical conformation were still present in the spectrum of poly-DL-leucine.

As noted above no low frequency far infrared absorption lines have been observed for PLA or PBLG although infrared active modes had been predicted in the 50 cm^{-1} region. In polymers of leucine and proline a broad absorption line observed at 65 cm^{-1} is attributed to skeletal

vibrations of the helical polymers. Definite assignment of the symmetry of the mode must await polarization studies, although this mode might tentatively be identified with the LA branch. In the case of poly-L-leucine this 65 cm^{-1} absorption is quite broad. An explanation of our inability to observe this mode in PLA or PBLG involves the disorder of these samples. The low frequency modes are affected by random interchain interactions that have been neglected in the normal mode calculations. These interactions broaden and shift the low frequency modes and invalidate the isolated helix model used in the normal mode calculations.

For several proteins and water soluble polymers only broad featureless absorption throughout the far infrared was observed. The problem of superimposed H_2O and polypeptide absorptions was discussed. The featureless absorption of the proteins can be understood in terms of the non-periodic (compared to homopolymers) protein structure which contains only short regions of α -helical conformation composed of amino acids with differing side chains.¹⁰⁹

APPENDIX A

FAR INFRARED IMPURITY MODES

Introduction of impurities into alkali halide crystals relaxes the $\vec{k} = 0$ conservation law and results in impurity induced absorption in the far infrared. The modes of absorption which result can be described as localized modes, resonant modes or gap modes.¹⁴⁶

Localized modes (discussed in Chapter III) are impurity modes that occur at frequencies greater than the maximum phonon frequency of the pure crystal. Gap modes occur at frequencies in the gap between the optic and acoustic phonon branches. Both localized and gap modes are characterized by narrow linewidths at 4.2°K. Resonant modes, on the other hand, usually have larger low temperature linewidths because they occur in the frequency region of the pure crystal's phonon density of states.

1. Cl⁻ Gap Mode in KI

We have measured the chlorine gap mode absorption in KI at twice the resolution previously used.¹⁴⁷ To obtain the absorption constant, spectra were measured for pure and doped 1 mm thick KI crystals at 1.2°K. The pure KI crystal was grown in the Cornell Materials Science Crystal Growing Facility while the KI + KCl crystal was

a nominally pure Harshaw grown crystal. Figure A-1 shows the absorption constant as a function of frequency observed with a Rayleigh resolution width of 0.109 cm^{-1} . The points shown are the data while the solid line represents a fit to the data using a combination of three Lorentzian absorption peaks. The Lorentzian curves are given by

$$\alpha_i = \frac{a_i}{\frac{(\omega - \omega_{oi})^2}{\Gamma_i^2} + 1}$$

and the total absorption is $\alpha = \alpha_1 + \alpha_2 + \alpha_3$ where the parameters for the curves are given in Table A-1.

TABLE A-1

Lorentzian Parameters for Cl^- Gap Mode in KI

Peak	$\omega_o(\text{cm}^{-1})^*$	$a(\text{cm}^{-1})$	$\Gamma(\text{cm}^{-1})$	$a\Gamma(\text{cm}^{-2})$
1	76.44	0.4	0.26	0.10
2	76.73	6.2	0.18	1.12
3	77.06	14.5	0.15	2.18

*See frequency correction below.

In the Table the product $a\Gamma$ which is proportional to the absorption strength of the various lines has been calculated. It was previously thought that the stronger chlorine doublet (Peaks 2 and 3) was caused by the Cl^{35}

Figure A-1. Cl⁻ impurity induced absorption in KI at 1.2°K. The data are represented by points and the solid line results from fitting the data with the sum of three Lorentzians (dashes).

and Cl^{37} isotopes which have a natural abundance of 3:1 respectively.¹⁴⁷ However this supposition is insufficient to account for the ratio of the absorption strengths of these lines which is closer to 2:1 by our high resolution measurements.

To explain this inconsistency it is necessary to consider both the isotope effect of the Cl^- impurity and of its K^+ nearest neighbors whose isotopes have a natural abundance ratio $\text{K}^{39}:\text{K}^{41} = 93:7$. The different isotopes of the K^+ nearest neighbors of the F-center gap mode in KI have been found to result in a triplet with a frequency splitting of $\approx 0.7 \text{ cm}^{-1}$ between adjacent members of the triplet.⁸⁰ Proceeding from low to higher frequencies, the expected absorption strengths of the lines were predicted to be in the ratio of 1:30:210, and fairly good agreement was obtained with the experimental results. These relative strengths can also be calculated from a simple one dimensional model in which none, one or two of the K^{39} isotopes are replaced by the K^{41} isotope.

Since chlorine and potassium have similar masses, we might expect similar isotope shifts to result for isotopic substitutions at the impurity or one of its nearest neighbor sites. Assuming that the isotope splittings are the same, we superimpose the Cl^- doublet and the K^+ triplet. Each of the Cl^- isotope lines is

assumed split by the K^+ triplet. The resultant quadruplet is shown at the right. Notice that

Total 1 : 33 : 300 : 630

the predicted ratios of the strengths of the three strongest absorption lines are close to the 30:324:630 relative absorption strength values obtained by scaling Q_T from Table A-1.

Furthermore the relatively large half-width of absorption line 2 may be explained in part by a slight inequality in the isotope shift for Cl^- and K^+ . For absorption line 2 the increase in linewidth relative to line 3 is 0.03 cm^{-1} which is 10% of the frequency separation of these two lines. The masses of the Cl^{37} and K^{41} substitutional isotopes responsible for line 2 also differ by 10%. In the one dimensional model ($K^{39} Cl^{37} K^{39}$) and ($K^{41} Cl^{35} K^{39}$) contribute to the absorption strength of absorption line 2 in the ratio 210:90 respectively as depicted in the diagram above. Although absorption line 1 appears broader than the other lines, its composition of $30:3 = (K^{41} Cl^{37} K^{39}) : (K^{41} Cl^{35} K^{41})$ is dominated by the absorption strength of ($K^{41} Cl^{37} K^{39}$). Higher Cl^- impurity levels would appear necessary to attempt observation of the weaker of these absorptions or of the line 0 corresponding to ($K^{41} Cl^{37} K^{41}$).

A correction for the finite source size must be made to calculate the actual frequency and linewidth of an

absorption line measured with an interferometer. To calculate the frequencies of the absorption lines a multiplicative correction of 1.0002 must be applied to the frequencies measured with the Michelson interferometer.⁵⁴ This corresponds to adding 0.02 cm^{-1} to frequencies near 80 cm^{-1} . Hence

$$\omega_{02} = 76.75 \pm 0.02 \text{ cm}^{-1}$$

$$\omega_{03} = 77.08 \pm 0.02 \text{ cm}^{-1}$$

which agree well with the values of 76.79 and $77.10 \pm 0.05 \text{ cm}^{-1}$ published elsewhere.¹⁴⁷

A correction of $\Gamma_s = 0.02 \text{ cm}^{-1}$ must be applied to the resolution width. The full width at half maximum of the scanning function $[\sin(\pi\omega L)/(\pi\omega L)]^2$ is given by

$$\Gamma_L = 0.88 \frac{1}{L} = 0.096 \text{ cm}^{-1}$$

where L is the optical path difference of the two arms of the interferometer and $1/L$ is the Rayleigh resolution width. This path length determined half-width is combined with the broadening from the finite aperture, and then the total width Γ_T is extracted from the observed linewidth. Assuming Lorentzian combination laws, we find that $\Gamma_T = \Gamma_L + \Gamma_s = 0.12 \text{ cm}^{-1}$ which is the linewidth of H_2O absorption lines at 80 cm^{-1} observed with the Michelson interferometer.¹⁴⁸ Subtracting this width from the measured width of Cl^- absorption line 3 gives

$$\Gamma_3 = 0.03 \text{ cm}^{-1} .$$

Gaussian combination laws (e.g. $\Gamma_T^2 = \Gamma_L^2 + \Gamma_S^2$) which have been advocated for interferometers because of the similarity of the scanning function to a Gaussian give¹⁴⁹

$$\Gamma_3 = 0.11 \text{ cm}^{-1} .$$

An estimate of the expected residual linewidth can be obtained by analogy with the comparison between the residual strain broadened linewidths of the R- and U-center zero-phonon lines described earlier in Chapter III. In the present case, the Grüneisen constants of the Cl^- gap mode and the U-center local mode are the same order of magnitude.¹⁵⁰ Assuming the defect induced strains in the KBr U-center and the $\text{KI}:\text{Cl}^-$ crystals are similar, we calculate that at $1.2^\circ\text{K} (\omega_0/\Gamma)_U = 1.4 \times 10^3 \approx (\omega_0/\Gamma)_{\text{Cl}^-}$ so that $\Gamma_{\text{Cl}^-} \approx 0.05 \text{ cm}^{-1}$. This result is the correct order of magnitude to account for the observed linewidth. To our knowledge there have been no previous attempts in the literature to measure the 4.2°K linewidths of gap modes in KI.

2. CN^- Gap Mode in KI

The second gap mode we have investigated at high resolution does not have an extremely small half-width as is characteristic of other gap modes and was previously observed only at low resolution.¹⁴⁶ Figure A-2 shows

Figure A-2. CN⁻ impurity induced absorption in KI at 1.2°K. The weak, narrow absorption lines result from impurities other than CN⁻.

the absorption constant at 1.2°K of KI doped with two different CN^- concentrations. The corrected center frequency of the CN^- gap mode is $80.76 \pm 0.05 \text{ cm}^{-1}$ while the half-width of the absorption line is calculated to be 1.14 cm^{-1} using a Gaussian combination law. There are several narrow lines on the side of the CN^- absorption line which have been found in data taken on several crystals to be unrelated to the CN^- absorption. These narrow lines are attributed to other impurities in the crystals, and the narrow width of these absorption lines is characteristic of gap modes. The observed absorption lines are listed in Table A-2 together with their assignments.

TABLE A-2

Gap Modes of Impurities Observed in
KI: CN^- Spectra

$\omega(\text{cm}^{-1})$	Impurity	Reference
78.8	-----	
83.5	Cs^+	146
84.8	-----	
86.2	OH^-	151
86.9	OH^-	151
88.0	-----	

Some comment is necessary about other absorption lines in the frequency region shown in Figure A-2 which

were attributed to OH^- by Renk. In this frequency region the only two absorption lines observed to scale together from sample to sample were the two OH^- absorptions listed in the Table. The other absorption lines of comparable strength mentioned by Renk result from other impurities (such as Cl^- for the 77 cm^{-1} absorption). The absorption line listed at 88.0 cm^{-1} is not observed in the Figure but appeared in other data. Although NO_3^- has an absorption line at 88.0 cm^{-1} , lower frequency lines attributed to NO_3^- are not present in the data and the 88.0 cm^{-1} mode remains unassigned. In near infrared studies of NCO^- impurities in KI at 100°K , absorption lines displaced from the main NCO^- absorption lines by 77.8 and 82.2 cm^{-1} have been observed.¹⁵² The corresponding 4.2°K far infrared modes may be shifted in frequency slightly with the 78.8 cm^{-1} mode in Table A-2 associated with the 77.8 cm^{-1} absorption line. However no absorption line that scales with the 78.8 cm^{-1} line has been observed in the 83 cm^{-1} region of the far infrared. Such an absorption line should be observed to correspond to the 82.2 cm^{-1} near infrared line.

A broad absorption on the low frequency side of the main CN^- absorption line is observed in Figure A-2. This absorption is present in both the 0.25% KCN and the 0.01% KCN samples. The broad absorption scales with the impurity concentration as can be demonstrated using the data shown in the Figure. Hence this absorption appears

to be associated with the CN^- impurity.

Finally, we return to the question of the large half-width of the 80.76 cm^{-1} CN^- impurity mode in KI. Two CN^- induced absorptions are expected in the gap region corresponding to motion along the axis of the CN^- molecule or perpendicular to it.¹⁵³ One possible explanation of the observation of only one mode is that the other mode is shifted into the reststrahl region. Another explanation concerns the rapid tunneling of the CN^- between the various [100] directions. Such rapid reorientation could result in the CN^- acting as if it were in a spherically symmetric potential well.¹⁵³ The 1.14 cm^{-1} width of the CN^- absorption line might then result from coupling with the tunneling levels which have energy level spacings in the 1 cm^{-1} region.¹⁵³ Although we measured the CN^- absorption down to 2 or 3 cm^{-1} , no absorption from these tunneling levels was observed in KI at 4.2°K .

3. Tl^+ Impurity Induced Absorption in RbBr and RbI

Figure A-3 shows the 4.2°K impurity induced absorption of RbBr and RbI with Tl^+ impurities. The measurements are limited to frequencies less than 66 cm^{-1} because of reststrahl absorption at higher frequencies. Noise shows up in the absorption spectra as oscillations in the absorption constant. The shape of the Tl^+ absorption in RbBr and RbI is similar to the Tl^+ induced absorption in KI.¹⁵⁴ The broad low frequency absorption

Figure A-3. Tl⁺ impurity induced absorption in RbBr and RbI at 4.2°K.

in RbI:Tl^+ has a peak at 47 cm^{-1} . At higher frequencies (60 cm^{-1}) a somewhat narrower peak in the absorption constant is observed. The RbBr:Tl^+ data also suggest the presence of a peak at higher frequencies but it was obscured by the reststrahl region.

It is well known that impurities that do not strongly perturb the crystal structure result in absorption that maps out the density of states of the pure crystal.¹⁵⁴ Because of the similarity of the observed spectra and the lack of any large resonances, it appears that the Tl^+ induced absorption is indicative of the density of states of the RbBr , RbI and KI crystals.

APPENDIX B

FAR INFRARED ABSORPTION OF MISCELLANEOUS ORGANIC COMPOUNDS

We have measured the far infrared transmission of a variety of organic compounds. These compounds include fatty acids, carbohydrates and nucleotides which are all of biological interest. The transmission spectrum of a high molecular weight sample of the synthetic polymer polyethylene oxide (polyox) was also measured. The fatty acids and carbohydrates were obtained from Fisher Scientific Company. The nucleotides were obtained from Miles Laboratories and their identification is given below. The polyox was supplied to us by Dr. R. E. Hughes and originally came from the Union Carbide Corporation. The samples were typically obtained in powdered form and compressed into paraffin pellets as described in Chapter IV.

1. Polyethylene Oxide

Polyox is a relatively simple synthetic polymer in which the chemical repeat unit is $(-\text{CH}_2\text{CH}_2\text{O}-)$. Many narrow absorption lines have been observed in the near infrared ($\omega > 700 \text{ cm}^{-1}$) on cooling polyox to liquid nitrogen temperatures.¹⁵⁵ The far infrared transmission spectrum of polyox at 4.2°K is shown in Figure 4-23. There are an abundance of low frequency far infrared

absorption lines observed in the spectrum and the absorption lines have relatively narrow linewidths. From previous results for the amino acids in Chapter IV, we expect that the presence of sharp far infrared absorption lines is indicative of crystalline order. This is indeed the case as confirmed by the narrow powder x-ray diffraction peaks shown in Figure 4-12 for polyox. This polymer is less complex than the polypeptides described earlier and apparently it assumes a better defined crystalline state than the polypeptides.

2. Fatty Acids

Most fatty acids fall into two categories depending upon whether or not their long hydrocarbon chain has a kink in it which results from double bonds ($-\text{CH}=\text{CH}-$). The fatty acids without such a kink are called saturated fatty acids while those with a kink are referred to as unsaturated fatty acids. The two fatty acids whose far infrared absorption we have investigated are shown schematically at the right. These fatty acids have the same hydrocarbon chain length. The saturated fatty acid is stearic acid and has the chemical formula $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ and the unsaturated fatty acid is oleic acid with the chemical formula $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$. Infrared absorption measurements on a

series of saturated fatty acids with 1 to 16 methylene repeat units have been reported previously in the 1400 to 200 cm^{-1} region.¹⁵⁶

The far infrared transmission spectra of stearic acid and sodium oleate at 4.2°K are shown in Figure B-1. The relatively narrow and numerous absorption lines of the stearic acid suggest that it has a better defined crystal structure than sodium oleate. This contention is supported by the powder x-ray diffraction data shown in Figure 4-12. The stearic acid has more and narrower x-ray diffraction peaks suggesting that the straight hydrocarbon chains are incorporated into crystal structures more easily than are the kinked hydrocarbon chains.

3. Carbohydrates

The carbohydrates or saccharides we have studied in the far infrared consist of various combinations of the D-glucose (dextrose) molecule shown at the right.

Far infrared spectra were run of the individual dextrose units, of two of the dextrose units covalently bonded together to form maltose and of starch in which many of the dextrose units are bonded together to form long chains. Previous studies of carbohydrates in the near infrared indicated a dependence of the absorption line-width on the degree of crystallinity of the carbohydrate.¹⁵⁷

Figure B-1. Transmission spectra of dextrose, maltose, stearic acid and sodium oleate.

Far infrared absorption spectra of glucose and related saccharides have been measured at 300°K and 4.2°K for frequencies greater than 50 cm^{-1} .¹⁵⁸ A significant increase in the number of absorption lines and a related decrease in linewidth are observed on cooling the samples.

Figures 4-24 and B-1 show the results of our far infrared transmission measurements at 4.2°K on dextrose, maltose and starch. Dextrose has very narrow far infrared absorption lines while maltose exhibits somewhat broader absorption lines as shown in Figure B-1. For starch, only broad comparatively featureless absorption is observed in Figure 4-24. These results are consistent with our earlier measurements on alanine oligomers in which the longer oligomers had less precisely defined crystal structure and consequently broader and fewer absorption lines. In starch the irregularly spaced covalent linkages between chains would be expected to broaden the far infrared absorption in analogy with the broadening resulting from nonperiodic protein structure discussed in Chapter IV.

4. Nucleotides

The nucleotides whose far infrared properties we measured were obtained from Miles Laboratories and are listed in Table B-1. Studies of nucleotides using Raman techniques have been conducted previously for frequencies greater than 500 cm^{-1} .¹⁵⁹ In our far infrared transmission measurements shown in Figure 4-24 only very broad,

rather featureless absorption is observed for ADP and Poly A at 4.2°K. This result is consistent with the expected lack of well formed crystals for these complex molecules.

TABLE B-1

Nucleotides Studied in the Far Infrared

Sample	Lot No.	M.W.
adenosine 5'-diphosphate tri- sodium salt (ADP)	6	
polyadenylic acid (Poly A)	72	>100,000

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