1982

FAR-INFRARED AND VACUUM ULTRA-VIOLET STUDIES OF VIBRATIONAL SPECTRA OF RARE EARTH DOPED FLUORITE CRYSTALS.

WILLIAM B. KOLASA

University of Windsor

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FAR-INFRARED AND VUV STUDIES OF VIBRATIONAL SPECTRA OF RARE EARTH DOPED FLUORITE CRYSTALS

by

WILLIAM BOLESLAUS KOLASA

A Dissertation submitted to the Faculty of Graduate Studies through the Department of Physics in Partial Fulfillment of the requirements for the Degree of Doctor of Philosophy at The University of Windsor

Windsor, Ontario, Canada
1981
TO MY WIFE AND FAMILY
ABSTRACT

Vacuum ultra-violet absorption spectra and far-infrared spectra (10 to 500 cm\(^{-1}\)) were obtained for Sr\(_2\)F\(_2\)::RE\(^{3+}\) and BaF\(_2\)::RE\(^{3+}\) systems. Vacuum ultra-violet spectra were obtained at liquid nitrogen and liquid helium temperatures. Far-infrared spectra were obtained at room temperature only and also included the CaF\(_2\)::RE\(^{3+}\) system. The rare earth impurities consisted of Ce, Pr, Nd, Dy, Ho and Er. Ce is omitted from the ultra-violet work. The concentrations of the dopants varied from 0.005% atomic to 0.1% atomic.

We find in the present work that Sr\(_2\)F\(_2\)::RE\(^{3+}\) and BaF\(_2\)::RE\(^{3+}\) systems possess vibrational modes with frequencies of 438 cm\(^{-1}\) and 405 cm\(^{-1}\), respectively. These frequencies are considerably higher than the maximum frequencies in their corresponding density of states curves and are designated as belonging to local vibrational modes. These frequencies are similar to the 485 cm\(^{-1}\) frequency of the CaF\(_2\)::RE\(^{3+}\) system and support the view that the 485 cm\(^{-1}\) frequency belongs to a local mode.

An analysis of the ultra-violet data shows that the 438 cm\(^{-1}\) and 405 cm\(^{-1}\) frequencies are independent of the RE\(^{3+}\) impurity in either host. The data shows that these two frequencies are also independent of the symmetry (charge compensation) of the samples. Different concentrations of dysprosium indicate that the frequencies are independent of the concentration of the same RE\(^{3+}\) impurity within a given host as well.
To obtain far-infrared data necessitated the development of a suitable operational system. A major portion of the present work was concerned with this development and low temperature far-infrared work was reserved for future studies.

Far-infrared transmission (absorption) and reflection studies were initiated in an attempt to observe the local mode frequencies of the CaF$_2$:RE$^{+3}$, SrF$_2$:RE$^{+3}$, and BaF$_2$:RE$^{+3}$ systems. All samples exhibited very little transmittance in the regions of interest. Spectra of samples with the same host are quite similar. Spectra of samples with different hosts possess the same general features but are shifted in wavenumber from host to host. Any absorption due to the RE$^{+3}$ impurities could not be reliably determined from any of the absorption spectra. Reflection spectra revealed the Reststrahlen bands of the host crystals.
ACKNOWLEDGEMENTS

First, I would like to thank my advisor, Professor M. Schlesinger, for his guidance and support. His relentless interest in this project and myself is greatly appreciated.

I am indebted to Dr. D. J. McKenney of our Chemistry Department for the loan of his microwave generator used in the present work.

I would like to thank the technical staff of the Physics and Chemistry Departments for their help and cooperation.

The typing of the first draft by my father-in-law, Mr. H. Toensfeldt, is sincerely valued.

I am extremely grateful to Mrs. J. Franklin and Mrs. P. Parungo for the typing of the final draft as well as all of the necessary and required preparation needed to produce the final copy.

I also would like to thank Mr. P. Keefe who was largely responsible for the preparation of the figures and spectra.

Finally, I would like to express my thanks and gratitude to my wife, Mary. I deeply appreciate the encouragement, support and love she has given me throughout these years.
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CHAPTER I
INTRODUCTION
I.1 **Introductory Remarks**

The rare earth elements are usually classified into two categories, the lanthanides and the actinides. The lanthanides are fifteen chemically similar elements commencing with lanthanum \((Z = 57)\) and ending with lutetium \((Z = 71)\). They are characterized by the absence of a completely filled \(4f\) shell of electrons. The actinides are another set of fifteen chemically similar elements commencing with actinium \((Z = 89)\) and ending with lawrencium \((Z = 103)\). These elements are characterized by the absence of a completely filled \(5f\) shell of electrons. As such, the rare earth elements comprise approximately 30% of the known elements and are an important part of the periodic table. On this basis alone, a study of these elements would be important.

The present work is restricted to a spectroscopic investigation of the lanthanides only. Furthermore, the extreme members of the lanthanides, lanthanum and lutetium, are omitted from consideration. This is due to the fact that lanthanum does not contain a \(4f\) electron while the triply ionized state of lutetium has a completely filled \(4f\) shell of electrons. Therefore, in the present work, the rare earth elements are those elements commencing with cerium \((Z = 58)\) and ending with ytterbium \((Z = 70)\). Any further reference to the rare earth elements in the present work will implicitly imply these thirteen elements only. Even so, these thirteen elements comprise approximately 13% of the periodic table. Furthermore, in the triply ionized state, to be described later, the electronic configuration of every lanthanide is the same as its corresponding actinide analogue and the
theoretical procedures developed for understanding the electronic properties of the lanthanides may be transferred to the actinides almost without modification (1).

I.2 Electronic Configuration of the Rare Earths

The electronic configuration of the neutral rare earth atoms are composed of (2):

1. A Xe electron core \((1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}, 5s^2, 5p^6)\);

2. A \(4f^N\) inner shell of electrons with \(N = 1\) for cerium and increasing to \(N = 14\) for ytterbium;

3. Two or three outer electrons \((6s^2\) or \(5d6s^2\)). Cerium and gadolinium have three outer electrons \((5d6s^2)\) while the other eleven rare earth elements possess two outer electrons \((6s^2)\).

It has been shown by Mayer (3) and others (4,5) that the increase in nuclear charge accompanying each additional electron as the \(4f\) shell is progressively filled causes a contraction of the \(4f\) eigenfunction. This contraction is so rapid that in neodymium the \(4f\) eigenfunction has its maximum inside the closed \(5s^25p^6\) shells of the xenon structure. As a result, the \(4f\) electrons are drawn towards the interior of the atom and the \(4f\) shell behaves as an inner shell. This also produces a reduction in ionic radii with increasing atomic number. This lanthanide contraction is the reason for the failure of the \(4f\) eigenfunctions to appreciably penetrate into the environment and the shielding provided by the closed \(5s^25p^6\) shell prevents any strong interaction of the \(4f\) electrons with their surroundings. Figure 1.1
Fig. 1.1 Radial charge distribution $P^2(r)$ as a function of $r$ for the 4f, 5s, 5p, and 6s orbitals of Gd$^+$. 
shows the radial probability densities (square of the radial wavefunctions) for several orbits based on nonrelativistic Hartree-Fock calculations by Freeman and Watson (6). Although these are for Gd$^{+1}$, they apply to all rare earth ions with minor changes (7) and indicate that the 4f orbits are really inner orbits.

The spectra of the neutral rare earths with even two or three electrons outside of the 4f$^N$ shell can be of very complex structure. For example, in praseodymium besides the normal 4f$^3$6s$^2$ configuration, other configurations such as 4f$^3$6s6p, 4f$^3$5d6s, and 4f$^4$6s are able to contribute to the observed spectrum. The triply ionized rare earths (RE$^{+3}$), however, possess a substantially simpler configuration which makes the corresponding spectral analysis less complicated.

The triply ionized rare earths are produced by the removal of the outer electrons and an additional 4f electron in certain cases. The RE$^{+3}$ ions consist of a Xe core with a 4f$^N$ inner shell of electrons with N = 1 for cerium and increasing by one to N = 13 for ytterbium. As previously mentioned, the 4f$^N$ shell is a well shielded inner shell for these ions and the observed spectra would be expected to consist of sharp lines. However, it is experimentally very difficult to produce only one state of ionization in the free ions. That is, ions with different degrees of ionization will exist with one another.

To overcome this difficulty, a suitable crystal lattice can be used in which the rare earths enter into the lattice structure in the triply ionized state as an impurity. Suitability
infers that the crystal is transparent in the \( \text{RE}^{3+} \) ion's spectroscopic regions of interest. It also implies that the \( \text{RE}^{3+} \) ion does not appreciably alter the lattice constants of the crystal in which it is embedded. In other words, the \( \text{RE}^{3+} \) ion and that for which it is substituted should be of comparable size. Such suitable crystals, for the present work, are calcium fluoride (CaF\(_2\)) and its related crystals, strontium fluoride (SrF\(_2\)) and barium fluoride (BaF\(_2\)).

1.3 Crystal Structure

The crystal lattice structure of CaF\(_2\) is face-centered cubic, with a basis of one Ca\(^{2+}\) ion at (0,0,0) and F\(^-\) ions at (1/4, 1/4, 1/4) and (3/4, 3/4, 3/4). If the Ca\(^{2+}\) ion is replaced by the Sr\(^{2+}\) ion or the Ba\(^{2+}\) ion, then the corresponding lattice structure of SrF\(_2\) or BaF\(_2\) is obtained. The lattice constants, in Angstrom units, of CaF\(_2\), SrF\(_2\), and BaF\(_2\) are 5.45, 5.86, and 6.18, respectively (8). Further references to the CaF\(_2\) structure will also apply to SrF\(_2\) and BaF\(_2\), unless otherwise noted. The CaF\(_2\) structure may be visualized as a cubic array of F\(^-\) ions at the corners with a Ca\(^{2+}\) ion at every other body center as illustrated in Figure 1.2 (a).

The rare earth ion enters the lattice substitutionally for the Ca\(^{2+}\) ion in the triply ionized state. The introduction of this extra positive charge requires a negative charge compensator to keep the crystal electrically neutral. Depending upon the initial growing conditions or subsequent heat treatment of the crystal, the type of charge compensator may be an O\(^{2-}\) ion.
a) UNDOPE

b) COMPENSATION BY INTERSTITIAL FLOURIDE

c) COMPENSATION BY SUBSTITUTIONAL O$^{2-}$

Fig.1.2 THE CALCIUM FLUORIDE LATTICE
an OH\textsuperscript{-} ion, an H\textsuperscript{+} ion or an addition F\textsuperscript{-} ion.

In Figure 1.2 (b), charge compensation is accomplished by an interstitial F\textsuperscript{-} ion in an empty cube adjacent to the rare earth ion. In this case, the presence of the charge compensator reduces the symmetry about the RE\textsuperscript{+3} ion from cubic to tetragonal. Weber and Bierig (9), Low (10), and others (11-14) have confirmed the presence of this type of charge compensation. If the interstitial F\textsuperscript{-} ion is located far away from the rare earth ion, the symmetry about the RE\textsuperscript{+3} ion is essentially cubic. This kind of charge compensation has also been verified for many of the rare earth ions by Low (10,15-17), Hayes and Twidell (18) and others (19-21).

Another means of charge compensation is shown in Figure 1.2 (c). In this case an O\textsuperscript{2-} ion replaces an F\textsuperscript{-} ion at one of the corners of a cube which contains the RE\textsuperscript{+3} ion. The symmetry about the RE\textsuperscript{+3} ion is reduced to trigonal by this type of charge compensation. Observation of this type of trigonal symmetry was reported by Low and Rosenberger (22), Vinokurov et al. (23) and Makovsky (24). Forrester and Hemptstead (25) had also observed trigonal symmetry, but were experimentally unable to distinguish between a substitutional O\textsuperscript{2-} ion or an interstitial F\textsuperscript{-} ion in a next nearest neighbour empty cube as the charge compensator. Trigonal symmetry produced by substitutional OH\textsuperscript{-} ions replacing O\textsuperscript{2-} ions has also been observed by Sierra (26) and McLaughlin and Newman (27).
1.4 Energy Levels

Exact solutions of Schrödinger's equation for such complex systems as that of the rare earth ions are not possible due to, among other things, the large number of terms involved. However, various methods have been extensively developed (1,28-33) for the calculation of the energy levels of such complex systems. These methods begin with an approximation to the true system in order to obtain its properties without undue complications. This approximation consists of omitting various interactions contained in the true system. Once the properties of the approximation are obtained, these interactions are then introduced as perturbations to the simplified system. This approximation is called the zero-order approximation and for complex atoms the most common zero-order approximation used for solving Schrödinger's equation is the central field approximation.

In the central field approximation, each electron is assumed to move independently in a spherically symmetric field produced by the nucleus and all the other electrons. For the N electrons of the $4f^N$ configuration of the RE$^{+3}$ ion, Schrödinger's equation in the central field approximation can be written as

$$\sum_{i=1}^{N} \left[-\frac{\hbar^2}{2m} \nabla_i^2 + U(r_i)\right] \psi_0 = E_0 \psi_0 \quad (1.4-1a)$$

where

$$\sum_{i=1}^{N} U(r_i) = -\sum_{i=1}^{N} \frac{Ze_i^2}{r_i} + \sum_{i<j} \frac{e^2}{r_{ij}} \quad (1.4-1b)$$
By choosing a solution of the form

$$\psi_0 = \sum_{i=1}^{N} \phi(a^i)$$

(1.4-2)

each electron moving in the central field \(U(r_i)\) will then satisfy equations of the type

$$[-\frac{\hbar^2}{2m} \nabla^2 + U(r_i)]\phi(a^i) = E(a^i)\phi(a^i)$$

(1.4-3)

where \((a^i)\) represents a set of quantum numbers \((n, l, m, \xi)\) which specify the state of a single electron in the central field and \(E(a^i)\) represents the energy required to remove the \(i\)th electron from the neutral atom. The normalized solutions for the bound states of equation (1.4-3) can be written as

$$\phi(a^i) = r^{-l} R_{n\xi}(r) Y_{lm\xi}(\theta, \phi).$$

(1.4-4)

The radial function \(R_{n\xi}(r)\) depends on the central field potential energy function \(U(r_i)\) and the spherical harmonics \(Y_{lm\xi}\) are defined by

$$Y_{lm\xi}(\theta, \phi) = (-1)^m \frac{(2\xi+1)(\xi-|m|)!}{4\pi(\xi+|m|)!} P^m_{\xi}(\cos \theta) e^{i m \phi}$$

(1.4-5a)

and

$$P^m_{\xi}(w) = \frac{(1-w^2)^{m/2}}{2^\xi \xi!} \frac{d^{m+1}}{dw^{m+1}} (w^2 - 1)^\xi$$

(1.4-5b)

The spin variables of the one-electron eigenfunction may be taken into account by introducing a spin coordinate which may equal \(\pm \frac{1}{2}\), and a spin function \(S\). The eigenfunctions defined in (1.4-4) then become

$$\phi(n\xi m_s) = S(m_s, \sigma) r^{-l} R_{n\xi}(r) Y_{lm\xi}(\theta, \phi).$$

(1.4-6)
Solutions of equation (1.4-1) with the inclusion of spin can now be written as

\[ \psi_0 = \frac{N}{\sqrt{N!}} \sum_{i=1}^{N} \phi(a^i) \]  \hspace{1cm} (1.4-7)

where \( a^i \) represents the quantum numbers \((n_l m_l m_s)\) of the \( i \)th electron. To satisfy the Pauli exclusion principle a linear combination of these solutions must be chosen such that the resulting wave functions are always antisymmetric with respect to the simultaneous permutations of the spin and spatial coordinates of any pair of electrons. The resulting antisymmetrical solution may then be written as

\[ \psi_0 = \frac{1}{\sqrt{N!}} \sum_{P} (-1)^P P \phi_1(a^1) \phi_2(a^2) \ldots \phi_N(a^N) \]  \hspace{1cm} (1.4-8)

where \( P \) represents a permutation of the electrons and \( P \) is the parity of the permutation with the summation extending over all the permutations of the \( N \)-electron coordinates. Equation (1.4-8) may equivalently be written in the form of a determinant as

\[ \psi_0 = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(a^1) & \phi_2(a^1) & \ldots & \phi_N(a^1) \\ \phi_1(a^2) & \phi_2(a^2) & \ldots & \phi_N(a^2) \\ \ldots & \ldots & \ldots & \ldots \\ \phi_1(a^N) & \phi_2(a^N) & \ldots & \phi_N(a^N) \end{vmatrix} \]  \hspace{1cm} (1.4-9)

Since each electron of the \( N \)-electron 4\( f^N \) configuration moves independently of the other electrons in the central field approximation, the corresponding eigenvalues of Equation (1.4-1) for all states of the 4\( f^N \) configuration are degenerate. That
is, all states of the $4f^N$ configuration have the same energy in the zero order central field approximation. The degeneracy of the $4f^N$ configuration, consisting of equivalent electrons, is given by $\binom{14}{N}$. Some of this degeneracy may be removed by the inclusion of the electrostatic repulsion between electrons and the spin-orbit interaction as perturbations to the zero order Hamiltonian. The Hamiltonian for the free ion may then be written as

$$H = H_0 + H_1 + H_2$$  \hfill (1.4-10)

where

$$H_1 = \sum_{i<j}^{N} \frac{2}{r_{ij}}$$  \hfill (1.4-11)

represents the repulsive electrostatic interaction between the electrons summed over all electron pairs and

$$H_2 = \sum_{i=1}^{N} s_i (\ell_i \cdot s_i)$$  \hfill (1.4-12)

represents the spin-orbit interaction. Other interactions such as spin-spin, spin-other-orbit, relativistic changes, etc. are omitted here as their effect is small in comparison to $H_1$ and $H_2$. If the ion is placed in a crystal, the crystal field will also act as a perturbation and cause a further removal of the degeneracy. However, due to the shielding of the $4f$ electrons by the $5s^2 5p^6$ electrons, the spin-orbit interaction is much larger than the influence of the crystal field. Therefore, the crystal field usually acts as a weak perturbation upon the ions. Finally, any remaining degeneracy may be removed by the application of an
external magnetic field upon the ions in the crystal.

Table I-1' (34) lists the four lowest configurations of the RE$^{3+}$ ions, the number of energy levels and the number of allowed transitions for the free ions including the effects of the repulsive electrostatic interactions and the spin-orbit interactions. As shown, the number of energy levels for the $4f^N$ configuration can be quite large and can exceed 3000 for the $4f^{N-1}$-5d configuration. This presents a problem of uniquely labelling the states of a given configuration since several states having the same LS quantum numbers frequently occur. Additional quantum numbers are needed to permit a separation of these states. Group theoretical methods proposed by Racah (30) have overcome this difficulty for the classification of the states in the $4f^N$ configuration for $N$ less than five, but recent theoretical contributions by Drake and Schlesinger and others (35) and references therein, show promise of making the states within the $4f^N$ as well as the $4f^{N-1}$-5d configuration manageable for $N$ greater than four.

I.5 Electronic Transitions

The electronic transition intensity between two states is defined as $I(aJJ_Z; a'J'J'_Z) = N(aJJ_Z)hc\bar{\nu}T(aJJ_Z; a'J'J'_Z)$ where $a$ represents all other necessary quantum numbers, $N(aJJ_Z)$ is the number of atoms in state $aJJ_Z$, $\bar{\nu}$ is the wave number of the transition, and $T(aJJ_Z; a'J'J'_Z)$ is the transition probability. The total transition probability depends upon the following three transition probabilities:
TABLE I-1
The Four Lowest Configurations of the RE\(^{+3}\) Ions

<table>
<thead>
<tr>
<th>RE(^{+3})</th>
<th>N</th>
<th>4f(^N)</th>
<th>4f(^{N-1})-5d</th>
<th>4f(^{N-1})-6s</th>
<th>4f(^{N-1})-6p</th>
<th>SUM</th>
<th>Allowed Transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>Pr</td>
<td>2</td>
<td>13</td>
<td>20</td>
<td>4</td>
<td>12</td>
<td>49</td>
<td>324</td>
</tr>
<tr>
<td>Nd</td>
<td>3</td>
<td>41</td>
<td>107</td>
<td>24</td>
<td>69</td>
<td>241</td>
<td>5393</td>
</tr>
<tr>
<td>Pm</td>
<td>4</td>
<td>107</td>
<td>386</td>
<td>82</td>
<td>242</td>
<td>817</td>
<td>54639</td>
</tr>
<tr>
<td>Sm</td>
<td>5</td>
<td>198</td>
<td>977</td>
<td>208</td>
<td>611</td>
<td>1994</td>
<td>306604</td>
</tr>
<tr>
<td>Eu</td>
<td>6</td>
<td>295</td>
<td>1878</td>
<td>396</td>
<td>1168</td>
<td>3737</td>
<td></td>
</tr>
<tr>
<td>Gd</td>
<td>7</td>
<td>327</td>
<td>2725</td>
<td>576</td>
<td>1095</td>
<td>4723</td>
<td></td>
</tr>
<tr>
<td>Tb</td>
<td>8</td>
<td>295</td>
<td>3006</td>
<td>654</td>
<td>1928</td>
<td>5883</td>
<td></td>
</tr>
<tr>
<td>Dy</td>
<td>9</td>
<td>198</td>
<td>2725</td>
<td>576</td>
<td>1095</td>
<td>4594</td>
<td></td>
</tr>
<tr>
<td>Ho</td>
<td>10</td>
<td>107</td>
<td>1878</td>
<td>398</td>
<td>1168</td>
<td>3549</td>
<td></td>
</tr>
<tr>
<td>Er</td>
<td>11</td>
<td>41</td>
<td>977</td>
<td>208</td>
<td>611</td>
<td>1837</td>
<td></td>
</tr>
<tr>
<td>Tm</td>
<td>12</td>
<td>13</td>
<td>386</td>
<td>82</td>
<td>242</td>
<td>723</td>
<td>42281</td>
</tr>
<tr>
<td>Yb</td>
<td>13</td>
<td>2</td>
<td>107</td>
<td>24</td>
<td>69</td>
<td>202</td>
<td>3733</td>
</tr>
</tbody>
</table>
\[ T_{\text{Dipole}} = \frac{64\pi^4}{3\hbar} \bar{v}^3 | \langle aJJ_Z | P | a'J'Z' \rangle |^2 \]  
(1.5-1a)

\[ T_{\text{Mag}} = \frac{64\pi^4}{3\hbar} \bar{v}^3 | \langle aJJ_Z | M | a'J'Z' \rangle |^2 \]  
(1.5-1b)

\[ T_{\text{Quad}} = \frac{32\pi^6}{5\hbar} \bar{v}^5 | \langle aJJ_Z | Q | a'J'Z' \rangle |^2 \]  
(1.5-1c)

where \( P, M, \) and \( Q \) are, respectively, the electric dipole, magnetic dipole, and electric quadrupole moment operators. Broer et al. (36) and Jorgensen and Judd (37) have shown that pure electric quadrupole transitions are unlikely to be observed in rare earth ion spectra. On the other hand, Van Vleck (38) and Broer et al. (36) have found that the intensities of electric dipole transitions of rare earth ions in crystals are noticeably greater than magnetic dipole or electric quadrupole transitions. This indicates that electric dipole transitions are primarily responsible for the observed spectra of \( RE^{+3} \) ions in crystals. Therefore, only electric dipole transitions will be taken into consideration, in the present work. Selection rules have also been derived for electric dipole transitions of \( RE^{+3} \) ions in crystals by Judd (39) and Ofelt (40). These rules take the following form:

\[ \Delta L = \pm 1, \quad \Delta S = 0, \quad \Delta L \leq 2, \quad \Delta J \leq 6. \]  
(1.5-2)

The first rule states that the \( 4f^N \) configuration can only interact with the \( 4f^{N-1}5d \) or \( 4f^{N-1}5g \) configuration. This rule, however, can be violated due to the influence of the crystal field in mixing states of opposite parity, to be described later. In the case of strong spin-orbit coupling, the second and third rules may also break down. With respect to the fourth rule, Ofelt (40) has
shown that this is the only selection rule for \( J \) and no transition violating this rule is known.

It follows from the transition probability for electric dipole transitions where \( P \), the electric dipole moment operator, is defined as

\[
P = -e \sum \frac{r_i}{r}
\]  

that only transitions between states of opposite parity are allowed. For the free ion, \( 4f-4f \) intra-configuration electric dipole transitions in the \( 4f^N \) configuration are, therefore, strictly parity forbidden. When the \( RE^{+3} \) ion is placed in a crystal, the influence of the crystal field mixes states of opposite parity allowing intra-configuration electric dipole transitions. This mixing of states is caused by the interaction of the \( 4f^N \) level with the remote states of opposite parity, such as \( 4f^{N-1}-5d \) or \( 4f^{N-1}-5g \). The wavefunction in a crystal field may be written as

\[
\psi = a\psi_0 + b\psi_1
\]  

consisting of a part \( \psi_0 \) with the parity of \( 4f^N \) and a part of \( \psi_1 \), of opposite parity, with \( a \) approximately equal to one and \( b \) much much less than one. Hoogschagen and Gorter (41) have empirically found that \( b \) is of the order of magnitude \( 10^{-3} \). Approximate calculations by Varsanyi and Dieke (42) and Judd (39) have also produced the same order of magnitude for \( b \). Due to the shielding of the \( 4f \) electrons by the \( 5s^25p^6 \) electrons and the relatively small mixing of states produced by the crystal field, the \( 4f-4f \) transitions are usually sharp line crystal spectra of low intensity.
The $4f-4f$ transitions of the $RE^{+3}$ ions in crystals occur in the near infra-red, visible, and ultra-violet regions of the spectrum. Being in the fairly accessible regions of the spectrum, experimentally the bulk of the work done in the past was concerned with these transitions.

Technological and experimental advances have extended the accessibility of the spectral region to the vacuum ultra-violet and far infra-red, and only within the past ten years has high spectral resolution been available in these regions. These advances have prompted the study of $4f-5d$ transitions of $RE^{+3}$ ions in crystals. The $4f-5d$ electric dipole transitions involve states of opposite parity and are not forbidden in the free ion or crystal. As such, these transitions produce intense spectral lines. From intensity considerations alone, it is usually possible to differentiate $4f-4f$ crystal spectra transitions from $4f-5d$ transitions.

In the crystal, the wavefunctions of the $4f^{N-1}-5d$ configuration overlap the wavefunction of neighbouring ions due to the less effective shielding of the $5s^25p^6$ electrons. This allows the $4f^{N-1}-5d$ configuration to interact with neighbouring ions and the crystal lattice. Broadened spectral lines may result from this interaction. However, enough sharp line spectral structure still remains for analysis and interpretation to be possible. The $4f-5d$ transitions of the $RE^{+3}$ ions in crystals consist not only of electronic transitions, but also electron-phonon interactions as well. The vibronics associated with these transitions can usually be grouped into three categories. First,
the electron-phonon interactions may involve the RE$^{+3}$ ion and its nearest neighbours, thereby producing a localized vibrational mode. Second, these interactions may involve the RE$^{+3}$ ion and the vibrational modes of the host crystal, producing non-localized or crystal modes of vibration. Finally, the electron-phonon interactions may involve the RE$^{+3}$ ion and its neighbouring RE$^{+3}$ ions, producing other localized modes. The complexity and type of electron-phonon interactions depend upon the amount of lattice distortion produced during the transition as well as on the degree of electron-phonon coupling with the lattice. The 4f-5d electronic transitions occur in the ultra-violet or vacuum ultra-violet regions of the spectrum while the vibrational modes are usually found in the far infra-red region of the spectrum.

I.6 Purpose of Present Work

The spectra of RE$^{+3}$ ions in crystals are an important example for the study of complex spectra and provide experimental data for the verification of quantum mechanical theories of complex systems. The present work is an attempt to investigate 4f-5d transitions in rare earth doped alkaline earth fluorides in the ultra-violet (UV), vacuum ultra-violet (VUV), and far infra-red (IR) regions of the spectrum. In the UV, VUV, and far IR regions, an attempt is made to study the influence of different hosts on the same RE$^{+3}$ ion as well as the influence of different RE$^{+3}$ ions on the same host. A study of the influence of different concentrations of the same RE$^{+3}$ ion on the same host is also attempted in the far IR region.
Since low temperature CaF$_2$ crystals doped with RE$^{+3}$ ions have previously been investigated in the UV and VUV regions here and elsewhere [(43) and references therein], the present work is concerned only with SrF$_2$ and BaF$_2$ crystals doped with RE$^{+3}$ ions in the UV and VUV regions. The choice of SrF$_2$ and BaF$_2$ as hosts is due to their relationship to CaF$_2$ as previously described. In this respect, low temperature studies of 4f-5d transitions of RE$^{+3}$ ions is fairly complete with regard to these three hosts. On the other hand, the far IR work is not nearly as complete. Due to the great amount of experimental work involved, only room temperature spectra have been obtained in the far IR region. The room temperature spectra are fairly complete in the far IR. However, since low temperatures produce structured spectra whereas room temperature does not, the conclusions from the far IR spectra in the present work are incomplete. In conclusion, it is hoped that the results of the present work provide for a better understanding of electron-phonon interactions, mutual interactions between RE$^{+3}$ ions, and the 4f$^{N-1}$-5d configuration.
CHAPTER II
ULTRA-VIOLET EXPERIMENTAL
II.1 Crystal Samples

The samples used in the present work were supplied by Optovac Inc. They consisted of SrF$_2$ and BaF$_2$ crystals doped with various concentrations of rare earth elements. The concentration varied from 0.005% atomic to 0.1% atomic. This concentration interval was selected so that the effects of dopant clustering could be avoided (1). The dopants were cerium (Ce), praseodymium (Pr), neodymium (Nd), dysprosium (Dy), holmium (Ho), and erbium (Er). The samples were cleaved from cylindrical pellets of 10 mm diameter and 4 mm height in which the crystallographic axes were randomly oriented. Sample thicknesses of approximately 0.50 mm were used to reduce intensity losses due to Rayleigh scattering.

The samples were placed in one window of a specially designed double window liquid helium cryostat. The cryostat is an integral part of a unique double beam spectrophotometer system developed by M. Schlesinger and T. Szczurek (2). The dimensions of each window are about 7 x 3 mm. The doped sample is placed in one window while a nominally pure host crystal of comparable thickness is placed in the other window. The dopant-free host crystal is used as a reference and for ratio measurements with respect to the sample. The similar thickness of the crystals for ratio measurements ensures proper intensities are used. It also eliminates effects due to unwanted trace impurities present in both crystals.
II.2 Instrumental Set-Up

The instrumental set-up is depicted in Figure 2.1. The main components are the light source, the scanning monochromator, the cryostat, the photomultipliers and associated electronics, the recorder, and the various mechanical pumps, diffusion pumps and associated valves used to produce and maintain the required vacuums.

The scanning monochromator is a McPherson Model 225. It is a one meter vacuum ultra-violet instrument with a 600 line per mm grating capable of scanning from approximately 300 Angstroms to 6,000 Angstroms at any one of twelve different scanning speeds. Automatic focusing is provided and the wavelength can be read directly in Angstroms. Automatic focusing consists of moving the grating along the bisector of the angle subtended by the slits while the grating is being rotated about a vertical axis tangent to its center. The rotation of the grating positions the desired wavelength at the exit slit. The movement of the grating along the bisector provides the focusing by keeping the exit slit on the Rowland circle.

The mechanical pumps and high speed diffusion pumps can maintain the pressure in the main chamber of the Model 225 at about $3 \times 10^{-7}$ torr. The main chamber vacuum is isolated from the entrance and exit slit chambers by externally controlled flap valves. The entrance and exit slit chambers can be pumped to a vacuum of less than 100 microns by an optional external mechanical pump prior to opening the flap valves to maintain main chamber vacuum integrity. The entrance and exit slit
1. Light Source  
2. Slit Chambers  
3. Monochromator  
4. Cryostat  
5. Photomultipliers  
6. Electronics  
7. Recorder  
8. Traps  
9. Diffusion Pumps  
10. Mechanical Pumps  

X = Valves

Fig. 2.1. Vacuum Ultra-Violet Experimental Set-Up.
chambers also have separate external controls for varying the slit widths from ten microns to two millimeters without disturbing the system vacuum. All chambers also have external air inlet valves.

II.3 Light Sources

The light sources were placed in a specially designed holder (Fig. 2.2) which could be bolted directly onto the entrance slit chamber. The holder could accommodate a maximum of four light sources and was designed to enable any one light source to be rotated into position without disrupting the vacuum of the system.

The cryostat was connected to a separate high vacuum supply. A lithium fluoride window placed between the exit slit chamber and the cryostat maintained the integrity of the separate vacuums. Special Plexiglass light guides vacuum sealed the cryostat from the photomultipliers (see reference II.2) enabling the photomultipliers to remain at atmospheric pressure. The cryostat vacuum was produced by a Veeco Model VS-9 mobile high vacuum pumping station capable of reducing pressure to the region of $10^{-7}$ torr.

The ultra-violet detecting and recording system is shown in Figure 2.3. Sodium salicylate is used as the scintillator and a matched pair of photomultipliers, followed by amplification stages, completes the detection system. The rate meter in the reference channel counts the number of photons in an interval of
Fig. 2.2 Ultra-Violet Lamp Holder
(a) side view
(b) top view
Fig. 2.3 Ultra-Violet Detecting and Recording System.
100 msec. The timing is provided by an external one kilohertz oscillator. The resultant count is then sent to the recorder via an RC filter. The reference channel record serves as a monitor of the lamp output as a function of time and wavelength. It may also be used for wavelength calibration by introducing impurities with known emission spectra. The main function of the reference channel, however, is to provide the timing for the sample channel for ratio measurements. The ratio meter counts the number of photons in the sample channel in the time required to count one hundred photons in the reference channel. The output of the ratio meter is, therefore, a measure of the transmittance of the dopant. This output is then sent to the recorder via an RC filter.

The light sources spanning the region of approximately 1100Å to 1800Å were prepared in our laboratory. Such a light source is shown in Figure 2.4. It is made from a quartz tube of approximately 15 cm in length and 1 cm in diameter. Lithium fluoride (LiF) is the window material and the appendix tube contains the gettering material. The tube is filled with argon, krypton, or xenon gas at a pressure of 200 torrs. Microwave excitation is used to produce the continua of the various gases (Fig. 2.5).

The xenon and krypton continua were discovered in 1954 by Tanaka and Zelikoff (3,4). The existence of the argon continuum was shown by Tanaka (5) in 1955. Wilkinson and Tanaka (6) proposed that the xenon continuum is due to transitions
Fig. 2.4  Ultra-Violet Lamp

Fig. 2.5  The continua of the heavy inert gases.
between the excited $^3\Sigma_u^+$ state and the unstable $^1\Sigma_g^+$ state of the xenon molecule. Tanaka (5) also applied the same explanation to the continua of argon and krypton due to the following reasons:

1. Argon, krypton, and xenon have similar electronic configurations in the excited and ground states. Thus, their molecular states should have similar characteristics.

2. The excitation energy is greater for lighter atoms so that the spectrum should shift to shorter wavelengths in going to the lighter atoms.

3. The intensity of the continua should follow the order xenon, krypton, and argon because the proposed transition is an intercombination transition ($S = 0$) which is more strictly forbidden for the lighter elements.

The expectations set forth in (2) and (3) above agree quite well with the observations (Fig. 2.5) as noticed by Tanaka.

II.4 Preparation of Light Sources

The apparatus depicted in Figure 2.6 was the means by which the light sources were produced. The LiF windows were epoxied to the lamps and the gettering material (metallic barium) was inserted in the appendices of the tubes prior to attaching the light sources to the apparatus. The bottle of the particular gas to be used was then attached. The base of the apparatus was attached to the Veeco pumping station previously mentioned, and heat coils were wrapped around the tubes to expedite outgassing. The entire system was pumped for approximately two days.
Fig. 2.6 Ultra-Violet Lamp Production Apparatus.
Prior to filling the lamps with the gas, the getters were fired by external heating. The getters were absolutely essential to reduce the amounts of impurities in the gas. Furthermore, the firing of the getters turned out to be the most crucial phase of the entire preparation. It was discovered that in order to produce usable lamps the getters had to be fired very slowly while pumping was maintained. When heat was first applied to the getters, it was observed that the vacuum pressure decreased significantly. This was probably due to outgassing of impurities already on the surface of the getter. If the vacuum pressure was allowed to decrease too rapidly, corresponding to firing the getters too quickly, the lamps produced were useless. This was, perhaps, due to a chemical reaction between the getter and the surface impurities in this case. The change of colour of the getter under these conditions also seems to indicate that a chemical reaction had taken place. However, no verification of these propositions has been attempted.

After the getters were fired, the apparatus was isolated from the vacuum system and the tubes were filled with gas to a pressure of approximately 200 torrs. The tubes were then sealed. Two light sources were produced at a time in case one source turned out unusable. Also, since the lifetime of a light source is approximately ten hours with continuous use, in case both sources are usable, a relatively fresh lamp is available when needed. In any event, producing two sources at once saved an enormous amount of time.
CHAPTER III
ULTRA-VIOLET RESULTS
III.1 Introduction

Absorption spectra of SrF$_2$:RE$^{+3}$ were obtained with the following dopants: Ce, Nd, Dy, Ho, and Er. Although the concentrations of the dopants were not necessarily the same, only one concentration value of any given rare earth dopant was used, except for dysprosium. Two concentrations of dysprosium dopant were used.

The BaF$_2$:RE$^{+3}$ absorption spectra were obtained with Ce, Pr, Nd, Dy, Ho, and Er as dopants. Only one concentration value of any given rare earth dopant was used.

All spectra were obtained at room temperature (RT) and liquid nitrogen temperature (LNT). RT spectra did not show any vibronic structure and, therefore, are not presented.

Spectra at liquid helium temperature (LHT) were obtained for Nd and Er dopants in both host crystals. An LHT spectrum was also obtained for SrF$_2$:Ho$^{+3}$.

III.2 General Spectral Observations (Figs. 3.1-3.19)

A cursory examination of the spectra reveals that they are quite complicated. The spectra are composed mainly of broad peaks superimposed upon wide bands with very few sharp peaks present. The amplitude of the broad peaks are, in general, small in comparison to the amplitudes of the wide bands. There is also a general tendency, for a given host, of the widths of the peaks to increase somewhat while their amplitudes decrease with increasing atomic weights of the dopants. The amplitudes of
corresponding peaks for the same rare earth dopant and concentration also tend to be smaller in the BaF$_2$:RE$^{+3}$ spectra than for SrF$_2$:RE$^{+3}$ spectra.

More zero phonon lines and sharp peaks occur in SrF$_2$:RE$^{+3}$ spectra than in BaF$_2$:RE$^{+3}$ spectra. The number and amplitudes of these sharp peaks also appear to diminish as the atomic weights of the dopants increase. In some BaF$_2$:RE$^{+3}$ spectra, zero phonon lines are either absent or hard to determine if present.

There also appears to be little change between LNT spectra and corresponding LHT spectra. Furthermore, there is a tendency of less change between LNT spectra and LHT spectra as the atomic weights of the dopants increase. The changes which do occur, however, are most evident in the vicinities of the zero phonon lines. LHT spectra also show a slight increase in the amplitude of the broad peaks, thus exhibiting more vibronic structure. However, a comparison of CaF$_2$:RE$^{+3}$ spectra with either SrF$_2$:RE$^{+3}$ spectra or BaF$_2$:RE$^{+3}$ spectra shows that the CaF$_2$:RE$^{+3}$ spectra possess sharper peaks and zero phonon lines of larger amplitude and fewer broad peaks [e.g. CaF$_2$ Ho$^{+3}$ (1)]. However, the gross appearances of the spectra are quite similar for the same rare earth dopant among the three host crystals.

III.3 Frequency Determination

The broadness of individual peaks as well as shapes of others presented problems in determining their wavelengths and, therefore, their corresponding frequencies (cm$^{-1}$). The broadness
of the peaks posed difficulties in determining the exact wavelengths of their peak amplitudes (i.e. the centers of the peaks). The shapes of some of the peaks, on the other hand, represent a superposition of at least two peaks which have not been completely resolved. Since any one of these resultant shapes may be represented by a superposition of a number of peaks of slightly different amplitudes and wavelengths, it is not possible in practice to resolve these into their actual components. As such, the assignment of wavelengths to these resultant peaks should be considered tentative. In any case, we estimate that with careful examination of the spectra, the vibronic frequencies are accurate to within about \( \pm 5 \text{ cm}^{-1} \).

The determination of vibronic frequencies with respect to zero phonon lines also presented difficulties. In comparison to CaF$_2$·RE$^{+3}$ spectra [e.g. see reference (1)], the zero phonon lines in the present work are, in general, of smaller amplitude and somewhat broader. This sometimes presented problems in identifying the zero phonon lines. Some spectra, on the other hand, do not appear to have any zero phonon lines. At least, no lines which can be positively identified as zero phonon lines by inspection. In such cases, the highest local mode phonon frequency was ascertained by an examination and comparison of the vibrational structure within a given wide band and the tentative assignment of zero phonon lines. There were also instances where only calculations of differences of phonon frequencies among adjacent peaks without regard for zero phonon lines presented the only feasible possibilities.
Fig. 3.1 Absorption spectrum of SrF$_2$:Dy$^{3+}$ (0.05% concentration) at LNT.
Fig. 3.2 Absorption spectrum of SrF$_2$:Dy$^{+3}$ (0.05% concentration) at LNT in the 1550-1750Å region. Some of the calculated local mode frequencies (cm$^{-1}$) are indicated.
Fig. 3.4 Absorption spectrum of SrF$_2$:Dy$^{+3}$ (0.1% concentration) at LNT in the 1550-1750Å region. Some of the calculated local mode frequencies (cm$^{-1}$) are indicated.
Fig. 3.5 Absorption spectrum of SrF$_2$:Nd$^{+3}$ (0.005% concentration) at LHT.
Fig. 3.6 Absorption spectrum of SrF₂:Nd⁺³ (0.005% concentration) at LHT in the 1700-1800Å region. Some of the calculated local mode frequencies (cm⁻¹) are indicated.
Fig. 3.7 Absorption spectrum of SrF$_2$:Nd$^{3+}$ (0.005% concentration) at LNT.
Fig. 3.8 Absorption spectrum of SrF$_2$:Nd$^{+3}$ (0.005% concentration) at LNT in the 1650-1800Å region. Some of the calculated local mode frequencies (cm$^{-1}$) are indicated.
Fig. 3.9 Absorption spectrum of BaF$_2$:Nd$^{3+}$ (0.01% concentration) at LHT.
Fig. 3.10  Absorption spectrum of BaF$_2$:Nd$^{+3}$ (0.01% concentration) at LHT in the 1500-1650Å region. Some of the calculated local mode frequencies (cm$^{-1}$) are indicated.
Fig. 3.11 Absorption spectrum of BaF$_2$:Nd$^{3+}$ (0.01% concentration) at LHT in the 1600-1800 Å region. Some of the calculated local mode frequencies (cm$^{-1}$) are indicated.
Fig. 3.13 Absorption spectrum of BaF$_2$:Nd$^{+3}$ (0.01% concentration) at LNT in the 1550-1800Å region. Some of the calculated local mode frequencies (cm$^{-1}$) are indicated.
Fig. 3.14  Absorption spectrum of SrF$_2$:Ho$^{+3}$ (0.1% concentration) at LHT. Some of the calculated local mode frequencies (cm$^{-1}$) are indicated.
Absorption spectrum of SrF₂:Ho³⁺ (0.1% concentration) at 1NT. Some of the calculated local mode frequencies (cm⁻¹) are indicated.

Fig. 3.15
Fig. 3.16 Absorption spectrum of SrF$_2$:Er$^{+3}$ (0.05% concentration) at LHT. Some of the calculated local mode frequencies (cm$^{-1}$) are indicated.
Fig. 3.17 Absorption spectrum of SrF$_2$:Er$^{3+}$ (0.05\% concentration at LNT. Some of the calculated local mode frequencies (cm$^{-1}$) are indicated.
Fig. 3.18  Absorption spectrum of BaF$_2$:Er$^{3+}$ (0.05% concentration) at LHT. Some of the calculated local mode frequencies (cm$^{-1}$) are indicated.
Fig. 3.19  Absorption spectrum of BaF$_2$:Er$^{3+}$ (0.05% concentration) at LNT. Some of the calculated local mode frequencies (cm$^{-1}$) are indicated.
III.4  **Analysis of SrF$_2$:Nd$^{+3}$ Spectrum**

We consider it worthwhile to present an example of the analysis of a spectrum. For this purpose an analysis of a portion of the SrF$_2$:Nd$^{+3}$ spectrum taken at LHT will be provided. Fig. 3.6 presents the absorption spectrum of SrF$_2$:Nd$^{+3}$ taken at LHT in the region from 1700-1800Å. The zero phonon peaks along with their respective vibronics are listed in Table III-1. There are also two peaks at 1756.7Å and 1743.4Å which are spaced from the first zero phonon peak at 1784.1Å by regular intervals of approximately 438 cm$^{-1}$. Thus, there are three series of vibronic structures which may be associated with the first zero phonon line. The first series extends from the zero phonon line at 1784.1Å to the first vibronic of approximately 438 cm$^{-1}$ at 1770.2Å. The second series starts at 1770.2Å and extends to 1756.7Å, while the third series covers the region from 1756.7Å to 1743.4Å. The peak at 1743.4Å designates the start of the fourth series. The vibronics associated with this fourth series cannot be reliably determined, however, due to their low intensities. The vibronic structure in the first series appears to be repeated, more or less, in the second and third series, although less pronounced.

The second zero phonon line at 1765.9Å also has two vibronic series of approximately 438 cm$^{-1}$. The first series extends from 1765.9Å to 1752.2Å, while the less pronounced second series spans the region from 1752.2Å to 1738.3Å. The second and third series of the first zero phonon line overlap the first and
second series of the second zero phonon line. Thus, the structure appears to be quite complicated. The structure in the first and second series of the second phonon line is, however, more pronounced than the overlapping second or third series of the first zero phonon line. Although less pronounced, the first series of the second zero phonon line resembles the first series of the first zero phonon line to a great extent.

The third zero phonon line at 1733.8 Å also exhibits a partial second series. The first 438 cm\(^{-1}\) series of the third zero phonon line begins at 1733.8 Å and ends at 1720.7 Å. The start of the second series is at 1720.7 Å. The end point of the second series cannot be determined due to the lack of vibronic structure. There does not appear to be any overlap from structure associated with either the first or second zero phonon lines with any series of the third zero phonon line. The vibronic structure of the first series of the third zero phonon line is also very similar to the first series of the second and first zero phonon lines.

Tables III-2 to III-6 represent a summary of the above. Tables III-2 lists the series extent and vibronics associated with each series for the three zero phonon lines. Tables III-3 through III-5 compare the frequency differences (cm\(^{-1}\)) within each series to those of the other series for each zero phonon line. Table III-6 is a comparison of frequency differences within the first series among the three phonon lines.

The agreement of the values among the tables is quite good and thus supports the proposed analysis. Most of the dis-
crepancies in the values can be ascribed to incorrectly labelling the wavelengths of the peaks as previously mentioned. The analysis of the rest of the SrF$_2$:Nd$^{3+}$ spectrum was done in much the same manner. The other spectra were also similarly analysed.

### TABLE III-1

Summary of absorption peaks in SrF$_2$:Nd$^{3+}$

(1700 - 1800Å at 4.2°K)

<table>
<thead>
<tr>
<th>Zero Phonon</th>
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<th>Vibronic</th>
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</thead>
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<tr>
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<td>$\nu$ (cm$^{-1}$)</td>
<td>$\lambda$ (Å)</td>
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<tr>
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<td>57677</td>
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</tbody>
</table>
TABLE III-2

Series and vibronics of zero phonon lines in SrF$_2$:Nd$^{4+}$ (1700 - 1800Å at 4.2°K)

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<th>Series</th>
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<th>$\nu$(cm$^{-1}$)</th>
<th>$\lambda$(Å)</th>
<th>$\nu$(cm$^{-1}$)</th>
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TABLE III-3

Comparison of frequency differences among series of first zero phonon line at 1784.1 Å in SrF₂:Nd³⁺ (1700 - 1800 Å at 4.2 °K)

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TABLE III-4

Comparison of frequency differences among series of second zero phonon line at 1765.9 Å in SrF₂:Nd⁺³
(1700 - 1800 Å at 4.2 °K)

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<td>57511</td>
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TABLE III-5

Comparison of frequency differences among series of third zero phonon line at 1733.8Å in SrF₂:Nd³⁺

(1700 - 1800Å at 4.2°K)

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### TABLE III-6

Comparison of frequency differences within first series among zero phonon lines in SrF\(_2\):Nd\(^{13}\)

(1700 - 1800\(\AA\) at 4.2°K)

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<th>(\Delta\nu(cm^{-1}))</th>
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CHAPTER IV

INFRARED EXPERIMENTAL
IV.1 Introduction

As previously mentioned, the 4f-5d transitions of the RE$^{3+}$ ions in the crystals of interest in this work are also accompanied by electron-phonon interactions. The corresponding vibronics occur in the far-infrared portion of the spectrum between approximately 100 and 500 cm$^{-1}$. A study of the far-infrared absorption spectrum of these crystals was considered necessary to gain a deeper insight of the mechanism by which these modes are excited. A comparison of the excited vibrational modes in the far-infrared to those excited in the vacuum ultra-violet could then be made. In the ultra-violet region, electronic transitions are accompanied by vibrational modes.

That is, vibrational modes are produced by the transition of the rare earth ion to an excited state. The energy of far-infrared radiation alone, however, is insufficient to raise the ion to an excited state. Hence, infrared radiation interacts with the ground state of the ion. A question then arises as to which vibrational modes, if any, excited in the vacuum ultra-violet region would also be excited in the far-infrared region. A comparison could, perhaps, provide information as to which modes are local modes of vibration and which are non-local. It would also provide information with respect to phonon-phonon and electron-phonon interactions produced in these crystals.

However, whereas there was a completely operational system available for the vacuum ultra-violet work, there was no such system available for the infrared work. Therefore, before
a far infrared study could be initiated, an operational system had to be developed and set up. Two prior acquisitions were available to form the bases of the system: A PDP-11/03 mini-computer manufactured by Digital Equipment Corporation and an FS-720 Fourier Spectrophotometer manufactured by Beckman Instruments, Inc. It was also realized that the development of the system was not a trivial task. As such, it was decided that the present work's objective would be to develop a thoroughly tested, operational system and obtain room temperature far infrared data. Although room temperature data was not expected to show much spectral structure, the realization of this data was considered a prerequisite for any additional work and is also the first step in any low temperature work. The next phase of obtaining far-infrared data at liquid nitrogen and liquid helium temperatures should be reserved for future work.

The development of the system was broadly partitioned into three phases or steps. The first phase consisted of becoming proficient in the use of the PDP-11. The second step dealt with satisfying the mechanical, electrical, and optical requirements of the interferometer. The integration of the computer and interferometer into an operational system constituted the final phase. This partitioning was somewhat arbitrary, but did provide a starting point as the initial stages of each phase could be considered, more or less, independent of the other phases. However, there was considerable overlap among the various phases which precluded a systematic completion of one phase before
the next phase was initiated. Rather, as the capabilities and requirements of each element to those of the total system became known, this influenced the manner in which the tasks of the various phases were performed. That is, as the knowledge of the components of the system increased, the concept of partitioning the system into phases became less and less meaningful. Finally, only the interactions of the components with respect to the requirements of the total system could be considered meaningful.

The first phase was not simply a matter of learning how to enter and run FORTRAN programs on the PDP-11. The initial requirements of the computer were threefold. First, it was to acquire the data from the interferometer. Second, it was to perform a fast Fourier transform on the data (to be described later). Third, it was to plot the resulting spectrum on the CRT monitor. The data acquisition routine could have been written in FORTRAN. This was undesirable, however, because it was not known what the sampling time requirements were at this point. Therefore, in order to provide the most efficient data acquisition routine possible in which timing considerations could be taken directly into account and controlled, this routine was to be written in assembly language. This required a thorough familiarity with the PDP-11 assembly language and the corresponding assembler directives, as well as a knowledge of how to switch between FORTRAN and assembly language and vice versa within a given program. This also necessitated assembly language control
and programming of the analog to digital converter, the real-time clock, and various input and output routines. Furthermore, a complete comprehension of the computer operating system and the computer architecture also had to be acquired.

The second phase of the development of the system was to produce an operational interferometer. That is, at the completion of this phase, sample data and timing pulses were to be in a form which could be accepted by the computer to produce a spectrum. This phase consisted of three parts: mechanical requirements, electrical circuits and proper optical components.

The mechanical requirements included assembling the peripheral hardware including the Golay detector. Then, vacuum and water lines had to be constructed and, finally, the system was tested for leaks. The interferometer also had to be physically near the computer and not subject to mechanical vibrations.

The electrical requirements were many. Pin assignments on all supplied cables had to be determined and matching cable connectors had to be acquired and subsequently mounted on a separate chassis. Power requirements for all motors, lamps, and the detector had to be ascertained, power supplies had to be ordered, and all associated wiring had to be completed. Although a rebuilt Moire amplifier was supplied with the interferometer, it was in need of repair and also required a separate fringe adjustment potentiometer and path difference selector switch to be added. The chopper signal had to be adapted for use with a lock-in amplifier. Various other switches and components were
also added as needed.

The major optical requirement was checking the optical alignment of the interferometer and making necessary adjustments. The alignment of the beam splitter was also checked as well as the adjustment of the Moiré gratings. Also, there were no specifications supplied by the manufacturer as to the usable frequency ranges of the interferometer's optical filters. Although these frequency ranges were subsequently determined, this problem was disconcerting since its solution required a complete operating system.

The third and final phase was the fusion of the various components into a complete operational system. In this phase the interferometer was interfaced to the computer and all required programs were written. All components and programs were thoroughly tested. The resultant absorption spectra obtained with water vapor samples were used as a test of the entire system by comparing them to known spectra.

Various decisions also had to be made before the system could be finalized. Among them was whether to use real-time analysis or off-line analysis (both will be described later). Initially, real-time analysis was chosen. However, a problem was encountered with this method which made this approach unacceptable. Subsequently, off-line analysis was adopted. There were two methods available for off-line analysis. One method made use of a single sided interferogram, while the other used a double sided interferogram. The double sided approach required twice the recording time, twice the computer memory
capacity, and about twice the computation time as compared to the single sided approach. However, the single sided approach required the computation of a function to correct for phase errors due to non-perfect interferometer alignment and due to sampling errors produced by not being able to sample at exactly zero path difference. With the double sided approach these errors are inherently eliminated. Since the double sided interferogram approach seemed easier and its drawback could be tolerated, this method was chosen for our off-line analysis.

It was also inevitable that a knowledge of Fourier transform theory had to be acquired in order to understand the requirements of the system. The application of the theory to the actual data acquired by the computer led, quite naturally, to the study of the discrete Fourier transform. This, in turn, with the realization that off-line techniques had to be employed led to a study of the fast Fourier transform (FFT). Furthermore, a recognition of the advantages of a Michelson interferometer over a grating spectrometer was also acquired. Finally, the experimental problems associated with obtaining usable data in the far-infrared region of the spectrum were also encountered and proper solutions were devised.

IV.2 Problems in the Far-Infrared

Experimentally, the far-infrared portion of the spectrum has always presented two major problems. First, the power available from far-infrared sources is very low and secondly, the detectors in this spectral region are severely limited by
noise. Since 1800, when Sir William Herschel separated the red from the infrared portion of the spectrum, until 1960 infrared and far-infrared radiation was derived from the incoherent emission of hot bodies. In the 1960's water vapor and hydrogen cyanide were made to lase in the far-infrared. Today there are many lasers providing emission lines in the far-infrared, but they are not tunable and, as such, are unusable for interferometry. The most frequently used source of far-infrared radiation is the high pressure mercury arc lamp enclosed in a thin quartz envelope. The mercury arc heats the quartz which then radiates in the far-infrared, but is opaque below about 50 micrometers (Figure 4.1).

In the far-infrared, the Raleigh-Jeans law is applicable; the power per square centimeter radiated by a blackbody at a temperature $T$ in a frequency interval $d\nu$ centered at a frequency $\nu$ is given by

$$P(\nu)d\nu = 8.6 \times 10^{-15}T\nu/\lambda^2$$

(4.2-1)

The power $P(\nu)d\nu$ is in watts, $T$ is in degrees Kelvin, $d\nu$ is in Hertz, and $\lambda$ is in micrometers. The emissivity of the source is taken as unity (i.e. blackbody). Figure 4.2 shows the power emitted in a 1 MHz band by a blackbody at 6000°K. This temperature is approximately that of a high pressure mercury arc. At best, in the region of interest, the radiated power is only about $10^{-7}$ or $10^{-8}$ watts. Even so, Stanevich et al. (1) have shown the superiority of the high pressure mercury arc in
Fig. 4.1  Transmittance of quartz

Fig. 4.2  Power radiated by 1 cm$^2$ of a blackbody at 600$^\circ$K in a bandwidth of 1 MHz.
this region of the spectrum over other solid radiators.

The essential capabilities of a detector can be specified by four quantities: the responsivity; the response time; the noise equivalent power; and the frequency range over which it is responsive. The responsivity of a detector is defined as the change in output signal per unit change of input power. The noise equivalent power (NEP) is defined as the quantity of radiation in watts which must fall on the detector to give out an rms electrical signal equal to the rms value of the noise. Essentially, the NEP is related to the power of the minimum detectable signal.

In general, three sources of noise may be distinguished in the far-infrared portion of the spectrum. First, background radiation incident on the detector due to the thermal emission by objects within the field of view of the detector. Second, noise arising within the detector. Third, noise associated with the amplification of the detector signal.

The interferometer used in the present work employed a Golay detector (Figure 4.3). This detector was introduced by M. Golay in 1947 (2). It uses an optical amplification method which gives it a high responsivity. The response of the detector is largely independent of the wavelength and the frequency range is determined by the window material. With proper choice of window materials it can operate from the ultraviolet to microwave wavelengths as long as 7.5 mm. The response time is rather long - between 2 and 3 msec and it has
Fig. 4.3 Golay detector.


Fig. 4.4 Luminous flux from an inclined source.
a NEP of about $10^{-10}$ watts for a 1 Hz bandwidth. In this detector the NEP is limited by noise due to Brownian motion. Although there are other far-infrared detectors available which have a lower NEP, the Golay detector is the only room temperature detector commonly used in this spectral region.

The detector operates as follows. Infrared radiation is passed through the window and absorbed by the absorbing film. The film transfers the heat to a gas in the cavity causing it to expand. Xenon is usually chosen as the cavity gas because of its thermal capacity and heat conductivity. The pressure of the gas is adjusted for best balance between sensitivity and response time. The expansion of the gas distorts a thin reflecting membrane. The reflecting membrane is positioned such that when it is not distorted no light reaches the photocell. Depending upon the amount of distortion of the membrane more or less light reaches the photocell whose signal is then amplified. A leakage path for the gas is provided around the reflecting membrane to compensate for slow temperature variations which would change the null position of the membrane-grid arrangement.

Besides the two major problems associated with sources and detectors, there is another experimental difficulty in the far-infrared. This is the strong absorption of far-infrared radiation by water vapor necessitating a vacuum environment for the interferometer and samples. For room temperature work a pressure of $10^{-3}$ torr is sufficient to eliminate the effects of
water absorption and can be supplied by a mechanical pump. When the sample is at liquid nitrogen temperatures and, even more so, liquid helium temperatures there exists the problem of condensation of contaminants on the sample, especially water vapor. A much higher vacuum which has to be provided through the use of diffusion pumps and traps is required to reduce these contaminants to an acceptable level. These requirements are more difficult to satisfy due to small leaks, outgassing, cryostat design, physical mounting of pumps and traps, etc. An example of a cryostat designed for use at liquid helium temperature is the one used in the present work in the vacuum ultraviolet region. The cryostat was designed by M. Schlesinger and T. Szczurek, and employs the use of a cold trap as part of the cryostat itself. The sample can be attached to the bottom of the inner chamber while a metal shield which surrounds the sample is attached to the outer chamber. The shield has openings which allow light to pass through the sample to the detector and serves as a cold trap for the sample. When liquid nitrogen is entered into the outer chamber, the shield is cooled. This causes contaminants to condense on the shield, including the contaminants within the shield in the region of the sample. When the sample is subsequently cooled to liquid helium or liquid nitrogen temperature, the contaminant condensation on the sample is greatly reduced with respect to the condensation which would occur without the shield.

The interferometer used in the present work is designed to be used at room temperature only. To use this instrument
at liquid nitrogen or liquid helium temperature would necessitate modifications and improvements of the vacuum seals.

IV.3 Comparison of Grating Spectrometer versus Michelson Interferometer

The optical arrangement of the instrument used in the present work is a Michelson interferometer. In the far-infrared portion of the spectrum the Michelson interferometer has many advantages as compared to a conventional grating spectrometer. Two of the most important advantages are known as the Fellgett or multiplex advantage and the Jacquinot advantage, also called the throughput or etendue.

The Fellgett advantage arises from the fact that an interferometer receives information about the entire spectral range at any given time, whereas the grating spectrometer receives information only in a narrow frequency band at any given time. This advantage may be explained as follows: The number of spectral elements \( M \) between wavenumbers \( \sigma_1 \) and \( \sigma_2 \) with resolution \( \delta \sigma \) is

\[
M = \frac{\sigma_2 - \sigma_1}{\delta \sigma} = \frac{\Delta \sigma}{\delta \sigma}
\]

If a grating spectrometer is being used, each small band of width \( \delta \sigma \) can be observed for a time \( T/M \) where \( T \) is the total time required for a scan from \( \sigma_1 \) to \( \sigma_2 \). The signal received in a small band \( \delta \sigma \) is then proportional to \( T/M \). If the noise is random and independent of the signal level, it can be shown by statistical methods or information theory (3) that the signal
noise is proportional to \((T/M)^{\frac{1}{2}}\). Therefore the signal to noise ratio is proportional to \((T/M)^{\frac{1}{2}}\).

An interferometer, however, detects all small bands of resolution \(\delta\sigma\) within the band \(\sigma_2 - \sigma_1\) all the time. The signal in a small band \(\delta\sigma\) is thus proportional to \(T\), the total scan time. If the noise is random and independent of the signal level, the signal noise is proportional to \(T^{\frac{1}{2}}\) with the same proportionality constant as for the grating instrument. The signal to noise ratio in this case is proportional to \(T^{\frac{1}{2}}\).

Therefore, the ratio of the signal to noise ratio of the interferometer to the signal to noise ratio of the grating spectrometer is equal to \(M^{\frac{1}{2}}\). Since \(M\) is the number of spectral elements in a broad band \(\sigma_2 - \sigma_1\), the interferometer has a much higher signal to noise ratio than the grating spectrometer. In the far-infrared region of interest in the present work, \(\sigma_2 - \sigma_1\) is of the order of the mean wavenumber \(\sigma\). \(M\) is then of the order of the resolving power \(R\) since \(R\) is defined as \(\sigma/\delta\sigma\) where \(\sigma\) is the mean wavenumber and \(\delta\sigma\) is the resolution. For instance, in the present work \(\sigma_2\) is approximately 500 cm\(^{-1}\) and \(\sigma_1\) is approximately 100 cm\(^{-1}\). \(\sigma_2 - \sigma_1\) is then 400 cm\(^{-1}\) and the mean wavenumber is 300 cm\(^{-1}\). \(M/R\) is then 1.33. Therefore, for high resolving powers of \(10^4\) to \(10^6\), the interferometer will have a better signal to noise ratio than the grating spectrometer by a factor of \(R^{\frac{1}{2}}\), or \(10^2\) to \(10^3\) for this case.

In the infrared region of the spectrum, the noise is usually detector noise, independent of the signal. Therefore,
the above arguments are valid in this region. However, in the visible region of the spectrum, photon noise of the source is dominant, due to better detectors in that region, and can be shown to be proportional to the square root of the source intensity. The noise is not independent of the source in the visible region of the spectrum and the Fellgett advantage is lost. However, the Jacquinot advantage is not affected.

The ability of the interferometers to collect large amounts of energy at high resolution as compared to grating spectrometers is known as the Jacquinot advantage. This advantage is a consequence of the fact that the brightness of an image is equal to the brightness of the object in a lossless optical system. Referring to Figure 4.4, the flux from a finite, inclined source striking an inclined collimator at a distance \( r \) from the source is

\[
dF = B(\cos \phi dS)(\cos \phi da)/r^2 \tag{4.3-1}
\]

where \( B \) is the brightness of the source. The flux may also be expressed as

\[
dF = B dA d\Omega. \tag{4.3-2}
\]

The etendue or throughput is defined as

\[
E = dF/B = dAd\Omega, \tag{4.3-3}
\]

and is a constant for an optical system with no losses. Now in order to compare the etendue of the Michelson interferometer to that of the grating spectrometer, expressions relating the resolutions to the solid angles are needed.
In the interferometer the maximum path difference is obtained by an axial ray and is equal to \( \delta = 2d \) where \( d \) is the distance between the movable mirror and the image of the fixed mirror. The path difference for non-axial rays is

\[
2d \cos \theta = \delta \cos \theta
\]  \hspace{1cm} (4.3-4)

and is smaller than the path difference for axial rays. Their difference is

\[
\Delta = \delta - \delta \cos \theta = \delta (1 - \cos \theta)
\]  \hspace{1cm} (4.3-5)

so that

\[
R = \frac{\delta}{\Delta} = \frac{1}{1 - \cos \theta}
\]  \hspace{1cm} (4.3-6)

where \( R \) is the resolving power. But the solid angle subtended by the source is defined as

\[
\Omega = \int_0^{2\pi} \int_0^\theta \sin \theta \, d\theta \, d\phi = 2\pi (1 - \cos \theta)
\]  \hspace{1cm} (4.3-7)

Therefore

\[
R\Omega = 2\pi
\]  \hspace{1cm} (4.3-8)

This last expression is due to Jacquinot (4,5) and gives the ultimate limit of resolution attainable with interferometers. This limitation, however, is not a serious restriction, for in practical instruments the largest solid angles used still permit resolving powers of several thousand. For instance, in astronomy, the source subtends such a small solid angle that essentially unlimited resolutions are allowed. The etendue of the interferometer can now be expressed as

\[
E = A\Omega = 2\pi A/R
\]  \hspace{1cm} (4.3-9)
For a grating spectrometer, with the exit slit in the focal plane of the collimator, the solid angle subtended by the exit slit is

$$\Omega = \frac{WL}{F^2} \quad (4.3-10)$$

where \(W\) is the width of the slit, \(L\) is its height, and \(F\) is the focal length of the collimator. The resolving power is given as

$$R = \frac{F}{W} \quad (4.3-11)$$

The etendue for grating spectrometers can now be expressed as

$$E = A\Omega = AL/RF \quad (4.3-12)$$

The ratio of the interferometer etendue to the spectrometer etendue is then equal to

$$\frac{E_I}{E_G} = \frac{2\pi F}{L} \quad (4.3-13)$$

assuming the same area and focal length of the collimators and the same resolving powers. In the best spectrometers, \(F/L\) is never less than 30 so that

$$\frac{E_I}{E_G} \approx 200. \quad (4.3-14)$$

This means that about 200 times more power can be put through the interferometer than through the best grating spectrometer. This characterizes the Jacquinot advantage.

Several additional advantages of the Michelson interferometer over the grating spectrometer can also be listed:

1. Very large resolving power
2. High wavenumber accuracy.
3. Vastly reduced stray or unwanted flux problems.
4. Large wavenumber range per scan.
5. Measurement of complex reflection or transmission coefficients by amplitude spectroscopy.
6. Low cost of basic optical equipment.
7. Smaller size and lower weight.

There are two main disadvantages of interferometers. The output of a Michelson interferometer is a record of intensity distribution versus mirror displacement called the interferogram. In order to obtain the spectrum the interferogram must be Fourier transformed. The second disadvantage is that a computer is required to Fourier transform the interferogram and computer costs must be considered as factors. However, with the advent and proliferation of minicomputers, the interferometer no longer has to have a dedicated computer. Thus, computer costs may be spread out over several experiments or projects.

Another disadvantage is that the interferogram usually cannot be easily interpreted. This makes it difficult to quickly judge whether or not the experiment is progressing satisfactorily. In some instances, this disadvantage may be overcome through the use of real-time analysis.

IV.4. Fourier Transform Spectroscopy

The concepts and theory of Fourier analysis were developed by J.B.J. Fourier in the early 1800's (6). Obviously, it is not a new topic and numerous articles and books have been published concerning Fourier analysis. It was, however, generally too
difficult to apply in many practical cases. Even with the advent of the modern digital computer, the application of Fourier transforms were still too time-consuming. Furthermore, computer time was expensive. Thus, for the most part, Fourier transform analyses remained more pedagogic than practical.

Then in 1965, Cooley and Tukey published a paper (7) describing a computational algorithm for Fourier transforms. The Cooley-Tukey algorithm drastically reduced the number of operations required to obtain a Fourier transform and has become known as the Fast Fourier Transform. After the Cooley-Tukey paper was published, it was realized that the idea they had "discovered" had already been worked out for hand calculators in 1942 by Danielson and Lanczos (8). Thus, Cooley and Tukey had actually rediscovered the algorithm, but had they not published their paper the fast Fourier transform might still be unknown today.

The advent of the fast Fourier transform has made possible many applications of Fourier transforms which hitherto had been impractical. These numerous applications are due to the versatile nature of the Fourier transform. For not only is the Fourier transform an important branch of mathematics, it is also applicable to a great variety of seemingly unrelated areas. Some of these areas are physics, optics, signal processing, probability, and antenna systems. There are also military applications of Fourier transforms in the area of communications. The military application is an ingenious use of the Fourier transform. In
order to illustrate the versatility of the Fourier transform, it is worthwhile to exemplify this application.

Consider a headquarters which must communicate with a number of outposts. Each outpost receives its information and commands on a different frequency. The headquarters transmits a signal which represents an intensity distribution as a function of displacement. That is, it transmits an interferogram. This signal contains all frequencies within a certain band including the outpost frequencies. Furthermore, the outpost frequencies can be individually amplitude modulated with each transmission. However, the only way individual frequency components may be selected from the transmitted signal is by means of a Fourier transform. The outposts perform a fast Fourier transform on the received signal and only monitor their own designated frequency. This provides one amplitude point at the designated frequency. Another signal is then sent by the headquarters which is again fast Fourier transformed by the outposts and provides a second point of a different amplitude at the monitored frequency. Subsequent signals are transmitted and fast Fourier transformed in the same manner. Upon completion, each outpost has a record of amplitude versus time at its particular frequency which constitutes the message. The time between signal transmissions from the headquarters corresponds to the time required for the outposts to perform the fast Fourier transform. The length of time of each transmission is determined by the frequency resolution required. The resolution, in turn, is determined by
the frequency separations of the outposts.

It would be highly unlikely that an enemy would have a knowledge of all outpost frequencies. Thus, it would be extremely difficult to prevent a message from reaching all outposts since this would require jamming of all frequencies during the entire time the message is transmitted. Even if one outpost frequency was known, however, it would still be difficult to jam or monitor by an enemy as provision would probably be made to change outpost frequencies every so often. Therefore, this is a very efficient and desirable method for military communications or for any communications which must be strictly private.

The area of application of the Fourier transform in the present work, however, is far-infrared spectroscopy. In particular, the interest is in the Fourier transform as it pertains to a Michelson interferometer. As such, a short presentation of Fourier spectroscopy, tailored to our application, is deemed appropriate.

In a Michelson interferometer one beam of a given amplitude is split in two beams of equal amplitude. The two beams travel different optical path lengths and then are recombined to produce an interference pattern. Let

\[ y_1 = A_0 \exp[i(\omega t - 2\pi \sigma X_1)] \quad (4.4.1) \]

and

\[ y_2 = A_0 \exp[i(\omega t - 2\pi \sigma X_2)] \quad (4.4.2) \]

represent two monochromatic beams of wavenumber \( \sigma \) and amplitude \( A_0 \) which have travelled optical path lengths \( X_1 \) and \( X_2 \). The
recombined beam is then

\[ y = A_0 \{ \exp[i(\omega t - 2\pi\sigma X_1)] + \exp[i(\omega t - 2\pi\sigma X_2)] \} \quad (4.4-3) \]

If \( \delta \) is defined as the path difference \((X_2 - X_1)\), then for polychromatic radiation the intensity as a function of \( \delta \) is given as

\[ I(\delta) = \int_0^\infty 2A_0^2(\sigma) \, d\sigma + \int_0^\infty 2A_0^2(\sigma) \cos(2\pi\sigma\delta) \, d\sigma \quad (4.4-4) \]

This can be written as

\[ I(\delta) = I(0)/2 + \int_0^\infty 2A_0^2(\sigma) \cos(2\pi\sigma\delta) \, d\sigma \quad (4.4-5a) \]

or

\[ I(\delta) = I(\infty) + \int_0^\infty 2A_0^2(\sigma) \cos(2\pi\sigma\delta) \, d\sigma \quad (4.4-5b) \]

By rearranging terms and setting \( B(\sigma) = A_0^2(\sigma) \), one has

\[ I(\delta) - I(0)/2 = 2 \int_0^\infty B(\sigma) \cos(2\pi\sigma\delta) \, d\sigma \quad (4.4-6a) \]

or

\[ I(\delta) - I(\infty) = 2 \int_0^\infty B(\sigma) \cos(2\pi\sigma\delta) \, d\sigma \quad (4.4-6b) \]

In a properly adjusted interferometer the intensity is a real, even function symmetric about zero path difference. As such, the intensity, \( I(\delta) \), and spectrum, \( B(\sigma) \), form a cosine Fourier transform pair such that

\[ I(\delta) - I(\infty) = 2 \int_0^\infty B(\sigma) \cos(2\pi\sigma\delta) \, d\sigma \quad (4.4-7a) \]

\[ B(\sigma) = \int_0^\infty [I(\delta) - I(\infty)] \cos(2\pi\sigma\delta) \, d\delta \quad (4.4-7b) \]

In order to obtain the entire spectrum, it is only necessary to repeat the calculation of the Fourier transform.
using Equation (4.4-7) for each wavenumber in the range of interest. This equation is the basic equation of Fourier transform spectroscopy.

The function \[ [I(\delta) - I(0)/2] \text{ or } [I(\delta) - I(\infty)] \] is usually called the interferogram and is the fluctuation of the signal about \( I(0)/2 \) or \( I(\infty) \). In some cases, however, the function \( I(\delta) \) alone is called the interferogram.

If the interferometer is not properly adjusted so that the function \( I(\delta) \) is not symmetric with respect to zero path difference (i.e., if it is not a truly even function), then the complex transform must be used,

\[
B(\sigma) = \int_{-\infty}^{\infty} [I(\delta) - I(\infty)] \exp(-i2\pi\sigma\delta)d\delta \quad (4.4-8)
\]

In an actual interferometer, the path difference obviously cannot extend from 0 to \( \infty \) (for a single sided interferogram) or from \( -\infty \) to \( +\infty \) (for a double sided interferogram). The path difference is limited to a finite maximum optical displacement \( L \). A monochromatic line, for instance, produces a cosine interferogram and vice versa. Now, consider what kind of spectrum would be obtained from an interferogram of a monochromatic source truncated between the limits of \( \pm L \). In this case the spectrum is given by

\[
B(\sigma) = \int_{-L}^{L} \cos(2\pi\sigma L) \cos(2\pi\sigma \delta)d\delta \quad (4.4-9)
\]

Thus

\[
B(\sigma) = 2L \left[ \frac{\sin 2\pi(\sigma L)}{2\pi(\sigma L)} \right] \quad (4.4-10)
\]
Defining \( Z = 2\pi(\sigma_1 - \sigma)L \) and sinc \( Z = \frac{\sin Z}{Z} \) results in

\[
B(\sigma) = 2L \text{sinc} Z
\]  

(4.4-11)

The function \( 2L \text{sinc} Z \) is called the instrument line shape function (ILS), the instrument function, or the scanning function. It is the function recorded at the output of the detector when an infinitely sharp spectral line of wavenumber \( \sigma \) illuminates the interferometer. The ILS is a consequence of a finite path difference and, thus, a property of any real instrument. An ILS is shown in Figure 4.5 along with the function \( \text{sinc}^2 (Z/2) \) to be discussed later. From the point of view of resolution, the ILS is not satisfactory as it stands because the secondary lobes ("feet") are so large in comparison to the main lobe. These features would tend to hide weak real lines in the vicinity of a strong line as well as appearing as false lines at nearby wavelengths. The size of the "feet" can be reduced by a process called apodization (from the Greek meaning "to take away the feet"). This process consists of introducing an apodization function \( A(\delta) \) so that \( B(\sigma) \) takes the form

\[
B(\sigma) = \int_{-L}^{L} \left[ I(\delta) - I(\infty) \right] A(\delta) \cos(2\pi\sigma\delta) d\delta. \tag{4.4-12}
\]

If the apodization function is the triangular function

\[
A(\delta) = 1 - \frac{|\delta|}{L}, \tag{4.4-13}
\]

then the spectrum of the monochromatic source would be

\[
B(\sigma) = \int_{-L}^{L} (1 - |\delta|/L) \cos[2\pi(\sigma_1 - \sigma)\delta] d\delta \tag{4.4-14}.
\]
Fig. 4.5  Plots of (1) sinc $Z$ and (2) $\text{sinc}^2\left(\frac{Z}{2}\right)$ versus $Z$. 
which upon integration yields

\[ B(\sigma) = L \frac{\sin^2(2\pi(\sigma_1 - \sigma)L)}{[2\pi(\sigma_1 - \sigma)L]^2} \quad (4.4-15) \]

or

\[ B(\sigma) = L \sin^2(Z/2) \quad (4.4-16) \]

where \( Z = 2\pi(\sigma_1 - \sigma)L \).

By comparing the \( \text{sinc} Z \) and \( \text{sinc}^2 (Z/2) \) functions in Figure 4.5, it can be seen that the apodization function has reduced the peaks of the "feet" by about a factor of four and negative intensities have been eliminated. The width of the central peak has also been increased somewhat, but not too seriously.

The effect of the instrument, then, is to limit the spatial extent of the monochromatic wave. That is, it truncates the wave in space. This truncated wave's Fourier transform is a spectrum consisting of a number of frequency distribution peaks. The most prominent peak is a narrow frequency distribution about the frequency of the monochromatic wave. The other peaks represent false frequencies.

The purpose of an apodization function is to remove these false frequencies from the spectrum. It does this by gradually reducing the amplitude of the truncated wave from its center to its ends such that the amplitude becomes zero at its boundaries. The apodization function transforms the truncated wave into a wave packet. The Fourier transform of this wave packet is a spectrum which is practically zero everywhere except for a narrow
frequency distribution peak about the frequency of the monochromatic wave. Thus, the false frequencies are eliminated from the spectrum.

The width of this frequency distribution peak depends upon the particular apodization function used to form the wave packet. That is the shape of the wave packet (i.e. Gaussian, triangular, sine, etc.) is related to the width of the peak. For any given truncated wave, however, the difference in shape among various wave packets is not very great. Therefore, the widths of their corresponding frequency distribution peaks will be about the same.

Thus, different apodization functions may be used, but there is not a great deal of difference in them as far as resolution is concerned. In practice, several apodization functions may be introduced in the computer and their effects on resolution can be determined one at a time. The function which gives the best resolution may then be selected as the one to be used. In effect, apodization decreases the peaks in the secondary lobes, but increases the width of the central peak causing a small degradation in the resolving power.

Not only is the path difference limited to a finite extent, but also in order to use a digital computer to perform the transform, the interferogram must be digitized. This is accomplished by sampling the interferogram at equally separated small path differences $\Delta \phi$ rather than continuously. In effect, it replaces the integral in the Fourier transform by a sum.
This process, however, introduces the so-called problem of aliasing and imposes a maximum wavenumber (or frequency) about which unambiguous information may be obtained with respect to the sampling interval.

The sampled interferogram may be related to the complete interferogram by the use of the shah or delta comb function such that

\[ I_s(\delta) = \text{comb}(\delta/\Delta\delta)I_c(\delta) \quad (4.4-17) \]

where \( \delta \) is the path difference, \( \Delta\delta \) is the sampling interval, \( I_s \) is the sampled interferogram, \( I_c \) is the complete interferogram, and \( \text{comb}(\ ) \) is the shah function. The shah function only picks out those values from the complete interferogram that occur at \( \delta = 0, \pm\Delta\delta, \pm 2\Delta\delta, \pm 3\Delta\delta, \ldots \) and is defined mathematically as

\[ \text{comb}(x) = \sum_{n=-\infty}^{\infty} \delta'(x-n) \quad (4.4-18) \]

where \( \delta'(x-n) \) is the Dirac delta function. From the definition of the shah function and the convolution theorem, one obtains

\[ \text{FT}^{-1}[I_s] = B_s(\sigma) = \sum_{n=-\infty}^{\infty} B_c[\sigma - n(\Delta\sigma)] \quad (4.4-19) \]

where \( \Delta\sigma = 1/\Delta\delta \).

The last result states that if the inverse Fourier transform of the sampled interferogram is computed, the entire spectrum is obtained every time \( \sigma \) equals \( n(\Delta\sigma) \) for all integers \( n \). That is, there is a duplicate spectrum starting at \( n(\Delta\sigma) \).

Whether or not there is an overlap of the repeated spectrum into the region from zero to some maximum value of \( \sigma \).
depends upon the magnitude of \( \Delta \sigma \). If the sampling interval, \( \Delta \delta \), is small, then \( \Delta \sigma \) will be large and no overlap will occur. If, however, \( \Delta \delta \) is large, then overlapping will occur and the true spectrum cannot be obtained from the sampled interferogram. This overlapping of the duplicate spectra onto the region of interest is called aliasing. Figure 4.6 is a reproduction of figures 7.1 and 7.2 from reference (9) and shows the effects of aliasing.

In order to prevent aliasing, \( \Delta \sigma \) must be large enough so that the maximum value of \( \sigma \) does not overlap with the imaged spectrum as can be seen from Figure 4.6. This may be satisfied by requiring that

\[
\sigma_{\text{max}} \leq \frac{1}{2 \Delta \delta}
\]  

(4.4-20)

This is also a direct consequence of information theory which states that in order to obtain unambiguous information the sampling interval must not be greater than one half of the shortest wavelength present. In other words, the highest frequency from which unambiguous information can be obtained is that which is sampled twice in a period of one cycle. This highest frequency, \( \sigma_{\text{max}} \), is called the alias frequency for the particular sampling interval. Spectral filters are the most commonly used means to eliminate frequencies greater than \( \sigma_{\text{max}} \) to prevent aliasing of the spectrum.

IV.5 Real-Time Analysis

There are basically two approaches to obtaining optical
Fig. 7-1. (a) Interferogram and (b) computed spectrum from a continuous, complete scan. The inverse Fourier transform of the interferogram in curve (a) would yield the two-sided spectrum in curve (b). One usually disregards the negative $\sigma$ spectrum, but in the sampling theory, one cannot ignore it.

Fig. 7-2. (a) Sampled interferogram. (b) Computed spectral components from the sampled interferogram. The solid line represents the positive $\sigma$ spectra from Fig. 7-1(b) and the dashed line represents the negative $\sigma$ spectra from Fig. 7-1(b). The total spectrum as would be computed from the sampled interferogram is shown in (c). The spectrum in (c) is the sum of the spectral components in (b).

Fig. 4.6 Effects of Aliasing.
spectra from interferograms: off-line analysis and real-time analysis. In off-line analysis, the spectrum is recovered after the complete interferogram is obtained. It will be discussed later. In real-time analysis, the spectrum is computed at each point of the interferogram while the interferogram is being obtained. That is, the contributions to all frequency elements of the entire spectrum are calculated at each sampled point of the interferogram.

The major advantage of real-time analysis is that any decisions regarding the progress of the experiment can be made during the measurement. Real-time analysis allows the experimenter to watch the spectral features develop as the mirror moves to larger displacements. As such, the experiment may be stopped when sufficient resolution has been obtained or if problems arise during the measurement. Thus, this approach can result in a large saving of time.

Real-time analysis, however, requires that a computer be available for the analysis while the experiment is running. This requires the interferometer to have either a dedicated computer to do the Fourier analysis or a general purpose computer located close to the instrument. The speed of the computer must also be great enough to perform the required calculations and the plotting of the spectrum in the time between sampling points of the interferogram. This usually necessitates slow scanning speeds. This, however, does not in general pose a serious problem in the far-infrared due to the slow response time of
detectors in that spectral region.

Due to the advantages of real-time analysis, this was the first method used to obtain spectra in the far-infrared in the present work. With this method the displayed spectrum began at a given wavenumber and consisted of $M$ frequency points spaced $\Delta \sigma$ apart. During the time required to measure a point on the interferogram, the contribution to the spectrum of the preceding point was calculated and the updated spectrum was plotted on the CRT monitor.

The procedure used was as follows. First, the average value of $I(\omega)$ was obtained. That is, the average intensity of the signal far away from zero path difference. Next, the path difference, the wavenumber increment, the starting wavenumber, and the number of points to be plotted were entered as parameters. The interferometer mirror was then positioned near zero path difference and the measurement began.

If the point at which zero path difference occurs is not sampled exactly, a linear phase error will result (7). A least squares parabolic fit to the interferogram points near zero path difference is utilized to correct for not sampling exactly at zero path difference. The interferogram is then sampled at the points $\delta = \varepsilon, \Delta \delta + \varepsilon, 2\Delta \delta + \varepsilon, \ldots$ instead of at $\delta = 0, \Delta \delta, 2\Delta \sigma, \ldots$ where $\varepsilon$ is defined in Figure 4.7.

The $k^{th}$ spectral element is given by

$$B(\sigma_k) = \sum_{j=0}^{N} S(j\Delta \delta + \varepsilon) \cos[2\pi \sigma_k (j\Delta \delta + \varepsilon)]$$  \hspace{1cm} (4.5-1)
Fig. 4.7 Parabolic fit of data points to determine zero path difference.

where \( S(j) = S(j \Delta \delta + \varepsilon) = I(j \Delta \delta + \varepsilon) - I(\infty) \)

\[ N = \text{number of points to be sampled,} \]

\[ (j \Delta \delta + \varepsilon) \text{ is the path difference,} \]

and \( \Delta \delta \) is the sampling interval.

The complete spectrum is then the sum of the \( B(\sigma_k) \) elements consisting of the \( M \) frequency points spaced \( \Delta \sigma \) apart. The computation consists of calculating

\[ B_j(\sigma_k) = B_{j-1}(\sigma_k) + S(j) \cos[2\pi \sigma_k (j \Delta \delta + \varepsilon)] \quad (4.5-2) \]

where \( B_0(\sigma_k) = S(0) \cos(2\pi \sigma_k \varepsilon) \) is the first spectral value calculated at \( \delta = \varepsilon \) for \( S(0) \). The resulting spectrum is then found by summing \( B_j(\sigma_k) \) for all \( k \) varying from zero to \( (M-1) \) and is then plotted on the CRT monitor. The entire procedure is done during the time it takes the interferometer to advance a distance \( \Delta \delta \) between sampling points. For instance, in our case two or three seconds were required to compute each 512 point spectrum. An additional five or six seconds were necessary to plot this spectrum on the CRT monitor. Thus, the total time required between sampling points was approximately eight seconds.

To simplify the computer calculations, the starting wavenumber is taken as an integer multiple of the wavenumber increment and the value of \( k \) is varied from zero to \( (M-1) \). The argument of the cosine can then be written as

\[ \theta(j,k) = (p + k)(jT + T_0) \quad (4.5-3) \]

where \( T \) and \( T_0 \) are constants for any given interferogram and are defined as:
\[ T = 2\pi\Delta\alpha\delta \quad (4.5-4a) \]
and
\[ T_0 = 2\pi\varepsilon\delta \quad (4.5-4b) \]

Appendix A contains a simplified flow chart and the computer program used for real-time analysis in this work utilizing the above concepts. The main body of the computer program was adapted from Appendix B of reference (9) with several important modifications made to suit our particular system. The modifications include, for instance, the data gathering and plotting routines. In addition, our programs have provision for plotting a ratioed spectrum in real-time. This is accomplished by calculating the ratio between the real-time spectrum just obtained with a previously stored spectrum. The previously stored spectrum may be a "no sample" background spectrum or a nominally pure host absorption spectrum.

Unfortunately, the real-time method presented a problem which made it impractical to continue with this method. Figure 4.8 is part of an interferogram about zero path difference with no sample in the interferometer. The interferogram is strongly modulated when our samples are inserted in the interferometer as shown in Figure 4.9. The intervals at which the modulations occur are less than our smallest available sampling interval. As such, the point at which zero path difference occurred could not be uniquely determined by any convenient or reliable means. The real-time method was, therefore, abandoned in favour of the off-line method utilizing a double sided interferogram which would not encounter this problem.
IV.6 Off-Line Analysis

Off-line analysis is characterized by the computation of the spectrum only after the entire interferogram has been acquired. As such, neither computational nor plotting time is required between sampled data points. Thus, faster scanning speeds can be used with this method than with real-time analysis. Substantial savings of instrument usage time are, therefore, possible. Also, as previously mentioned, off-line analysis of double sided interferograms eliminates the need to correct for not sampling exactly at zero path difference (7).

However, a major drawback of off-line analysis used to be the amount of time required to compute the spectrum. Consider, for instance, a double sided interferogram sampled at equal intervals of path difference. The basic equation of Fourier transform spectroscopy in a suitable form for numerical calculations may be written as

\[
B(\sigma_k) = \sum_{j=-N/2}^{N/2-1} A(j \Delta \delta, L)[I(\delta)-I(\omega)] \exp(-i2\pi \sigma_k j \Delta \delta) \quad (4.6-1a)
\]

\(A(j \Delta \delta, L)\) is an apodization function and \(N\) is the number of points to be sampled spaced \(\Delta \delta\) apart.

Defining \(S(j) = A(j \Delta \delta, L)[I(\delta)-I(\omega)]\), we can write

\[
B(\sigma_k) = \sum_{j=-N/2}^{N/2-1} S(j) \exp(-i2\pi \sigma_k j \Delta \delta) \quad (4.6-1b)
\]

The two forms of Equations (4.6-1) are often called discrete Fourier transforms (DFT). This is so since the spectral analysis of sampled data is a summation only over a finite range.
As can be seen from Equations (4.6-1), N does not have to be too large before computational problems arise in obtaining the DFT of a function. In fact, most applications of Fourier transform spectroscopy were impossible until the advent of fast digital computers. From the DFT of $B(\sigma_k)$ it can be seen that there are N complex additions to be performed for each $\sigma_k$. If there are N values of $\sigma_k$, then approximately $N^2$ operations are required to obtain the spectrum. For example, if there are 512 points to be transformed, then $N^2$ equals 262,144. The Cooley-Tukey fast Fourier transform (FFT) is an algorithm which reduces the number of operations from $N^2$ to $N \log_2 N$. The ability of the FFT to achieve this reduction is due to the utilization of the periodicity of the exponential function to eliminate redundant operations. For the 512 point transform, the number of operations is reduced from about 260,000 to about 5,000!

The basic idea of the FFT algorithm is that for each value of $\sigma_k$ the N point transform is split into two $N/2$ point transforms. Each of these $N/2$ point transforms is then split into two $N/4$ point transforms, and so on, until there are N 1-point transforms. Each N point transform, then, requires $\log_2 N$ splittings to reduce it to N 1-point transforms. If there are N values of $\sigma_k$, then the total number of operations is $N \log_2 N$. At any stage in this splitting process, the resultant two subsets may be combined to generate the transform of the previous stage. As will be shown, this combination involves one addition and one multiplication. It is in this combination
that the periodicity of the resultant exponential function is used to eliminate redundant operations. This is the key to the time saving involved in the FFT.

This entire procedure of using the FFT to obtain the \(N\) spectral elements of an \(N\) point DFT may be summarized as follows. First, the \(N\) point DFT representing \(B(\sigma_k)\) is split into two \(N/2\) point DFTs. These \(N/2\) point DFTs could be combined, utilizing the periodicity of the exponential function, to generate the original \(N\) point DFT. Each of these \(N/2\) point DFTs, however, are now split into two \(N/4\) point DFTs. Using the periodicity of the resulting exponential functions, these \(N/4\) point DFTs can be combined to recover the preceding \(N/2\) point DFTs. The \(N/2\) point DFTs are then used as just described to generate the original \(N\) point DFT. The \(N/4\) point DFTs, however, are now split into \(N/8\) point DFTs and so on, until \(N\) 1-point DFTs are produced.

These \(N\) 1-point DFTs provide the starting point from which the required spectrum is obtained. The 1-point DFTs are combined in pairs to produce \(N/2\) 2-point DFTs. These 2-point DFTs are then combined to produce \(N/4\) 4-point DFTs. These are then combined to produce \(N/8\) 8-point DFTs, and so on, until one \(N\)-point DFT is generated. If this entire process is repeated \(N\) times, then the \(N\) spectral elements of \(B(\sigma_k)\) are generated. At each combinational stage the periodicity of the exponential function is used to eliminate redundant operations. For each spectral element the number of combinations equals the number of splittings, \(\log_2 N\). The total number of combinations for \(N\)
spectral elements is \( N \log_2 N \), the total number of splittings.

The FFT algorithm in its usual form can transform an arbitrary complex function so that there is no restriction on the DFT. It is also desirable to have the number of sampled points be a power of two as this helps in the splitting process. The length of the computer program can also be very short (about 20 lines of FORTRAN) if the number of points is a power of two. This is especially important in applying the FFT to minicomputers in laboratory applications. In contrast, the IBM general purpose FFT FORTRAN program for an arbitrary number of points of complex multidimensional data is about 500 lines long.

The FFT technique may be illustrated by slightly modifying Equation (4.6-1b). The modifications render the equation more suitable for computations. To do this, let \( \sigma = k \Delta \sigma \) where \( 0 \leq k \leq (N-1) \) for \( N \) spectral elements. Also set \( B(\sigma_k) = B(k \Delta \sigma) = B(k) \).

Using the anti-aliasing relationship

\[
\sigma_{\text{max}} = \frac{1}{2 \Delta \sigma} \quad (4.6-2a)
\]

and the fact that

\[
\sigma_{\text{max}} = (N/2) \Delta \sigma \quad (4.6-2b)
\]

for \( (N/2) \) spectral elements, Equation (4.6-1b) can be rewritten as

\[
B(k) = \sum_{j=0}^{N-1} S(j) \exp(-i2\pi jk/N) \quad (4.6-3)
\]

The first step in applying the FFT algorithm to
Equation (4.6-3) is to split the complex elements of $S(j)$ into two sets. One set will be composed of the $S(j)$s with even $j$ indices, the other with odd $j$ indices. In so doing, we define

$$Y(j) = S(2j)$$  \hspace{1cm} (4.6-4a)
$$Z(j) = S(2j+1)$$  \hspace{1cm} (4.6-4b)

for $j = 0, 1, 2, 3, \ldots, (N/2)-1$

where $Y(j)$ and $Z(j)$ are complex functions.

Then

$$B(k) = \sum_{j=0}^{N/2-1} Y(j) \exp(-2\pi jk/[N/2]) + Z(j) \exp(-i2\pi jk/N) \exp(-i2\pi jk/[N/2])$$  \hspace{1cm} (4.6-5)

Now define

$$\text{DFT}[Y(j)] = C(k) = \sum_{j=0}^{N/2-1} Y(j) \exp(-i2\pi jk/[N/2])$$  \hspace{1cm} (4.6-6a)
$$\text{DFT}[Z(j)] = D(k) = \sum_{j=0}^{N/2-1} Z(j) \exp(-i2\pi jk/[N/2])$$  \hspace{1cm} (4.6-6b)

$$W(k) = \exp(-i2\pi k/N)$$  \hspace{1cm} (4.6-6c)

If $k$ is restricted to the interval $0 \leq k < N/2$, then Equation (4.6-5) can be expressed as

$$B(k) = C(k) + W(k)D(k)$$  \hspace{1cm} (4.6-7a)

for $0 \leq k < N/2$.

The other half of the spectrum may also be generated using the same $C(k)$ and $D(k)$. That is, no further computations are necessary to obtain the rest of the spectrum. This is due to the periodicity of $C(k)$, $D(k)$, and $W(k)$. Utilizing this periodicity, we can express
\[ B(k + N/2) = C(k) - W(k)D(k) \]  \hfill (4.6-7b)

for \( 0 \leq k < N/2 \).

Thus, the work of computing an \( N \) point DFT has been reduced to computing two \( N/2 \) point DFTs. Using the periodicity of the exponential functions, these \( N/2 \) point DFTs can be combined to generate the original \( N \) point DFT. Also, each combination involves one addition and one multiplication. If the same procedure is applied \( \log_2 N \) times, we can obtain the entire spectrum in \( N \log_2 N \) operations instead of \( N^2 \) operations.

Figures 4.10 taken from reference (10) illustrate this technique using eight input points. Figure 4.10a illustrates the classical DFT giving the eight outputs from the eight inputs. Figure 4.10b the eight values of \( S(j) \), designated as \( I(0) \) through \( I(7) \), have been split into two subsets \( P_1 \) and \( P_2 \), corresponding to the even and odd indices of \( S(j) \). To each of these subsets a DFT is applied and the operations described by Equation (4.6-7) give the final eight outputs of \( B \). For example,

\[ B(1) = C(1) + W(1)D(1) \]  \hfill (4.6-8a)

and

\[ B(6) = B(2 + 4) = C(2) - W(2)D(2) \]  \hfill (4.6-8b)

In Figure 4.10c the four input values of \( P_1 \) have been split into \( P_3 \) and \( P_4 \), while the four input values of \( P_2 \) have been split into \( P_5 \) and \( P_6 \). These represent the even and odd sets of \( P_1 \) and \( P_2 \). In this case, the operations described by Equation (4.6-7) have to be applied twice to obtain the eight outputs of \( B \). For instance,
Fig. 4.10 (a-d) Fast Fourier Transform
Graph for 8 Data Points.
\[ C(1) = E(1) + W(2)F(1) \quad (4.6-9a) \]
\[ D(1) = G(1) + W(2)H(1) \quad (4.6-9b) \]
\[ C(2) = C(0 + 2) = E(0) - W(0)F(0) \quad (4.6-9c) \]
\[ D(2) = D(0 + 2) = G(0) - W(0)H(0) \quad (4.6-9d) \]

(The Ws are defined with respect to N = 8 instead of N = 4.) If these values are now substituted in Equation (4.6-8), the spectral elements \( B(1) \) and \( B(6) \) will be generated.

Figure 4.10d shows the final result after each of the two input values of \( P_3 \), \( P_4 \), \( P_5 \), and \( P_6 \) are split. In this case, three applications of Equation (4.6-7) are necessary to obtain the eight outputs of \( B \). For our example, in terms of the input values of \( I \), the first application would yield

\[ E(0) = I(0) + W(0)I(4) \quad (4.6-10a) \]
\[ E(1) = E(0 + 1) = I(0) - W(0)I(4) \quad (4.6-10b) \]
\[ F(0) = I(2) + W(0)I(6) \quad (4.6-10c) \]
\[ F(1) = F(0 + 1) = I(2) - W(0)I(6) \quad (4.6-10d) \]
\[ G(0) = I(1) + W(0)I(5) \quad (4.6-10e) \]
\[ G(1) = G(0 + 1) = I(1) - W(0)I(5) \quad (4.6-10f) \]
\[ H(0) = I(3) + W(0)I(7) \quad (4.6-10g) \]
\[ H(1) + H(0 + 1) = I(3) - W(0)I(7) \quad (4.6-10h) \]

(The Ws are defined, once again, with respect to N = 8.) The second application corresponds to the substitution of Equation (4.6-10) into Equation (4.6-9). The substitution of these subsequent results into Equation (4.6-8) constitutes the third application and generates \( B(1) \) and \( B(6) \). The other spectral elements are obtained in a similar manner. Thus, three
applications of Equation (4.6-7) per point, corresponding to
3 = \log_2 8, yield the eight spectral elements of an eight point
DFT.

It must be noted that the signal flow graph of Figure
4.10a represents Equation (4.6-7) and Figure 4.10d is an identical
representation of the true DFT (Equation 4.603). That is, the
FFT is not an approximation, but a method of computation which
reduces the work by recognizing symmetries and by not repeating
redundant operations. Therefore, the accuracy of the result is
not reduced by use of the FFT.

To obtain an ordered output set of B(k) the input set
of S(j)s must be sorted, as shown in Figure 4.10d for eight input
S(j)s. The process by which the initially ordered set of S(j)s
are put into the proper order is called binary bit inversion.
This can be illustrated using the eight point example. The first
column of Table IV-1 shows the initially ordered set of S(j)s
with j written in binary form (with \log_2 N bits). The second
column represents the binary numbers formed by inverting the bits
of the first column. The resulting S(j)s in the second column
are in precisely the correct order to be used with the FFT, as
reference to Figure 4.10d will show. Thus, in order to produce
an ordered output set of B(k), the initially ordered set of
S(j)s must be put into their proper binary bit inverted order
before the FFT is applied.

The procedure just described assumed that the S(j)s
were complex numbers and required storage locations for N complex
numbers. The interferogram, however, is a real function and if
### TABLE IV-1

**Binary Bit Inversion**

<table>
<thead>
<tr>
<th>S(0)</th>
<th>000</th>
</tr>
</thead>
<tbody>
<tr>
<td>S(1)</td>
<td>001</td>
</tr>
<tr>
<td>S(2)</td>
<td>010</td>
</tr>
<tr>
<td>S(3)</td>
<td>011</td>
</tr>
<tr>
<td>S(4)</td>
<td>100</td>
</tr>
<tr>
<td>S(5)</td>
<td>101</td>
</tr>
<tr>
<td>S(6)</td>
<td>110</td>
</tr>
<tr>
<td>S(7)</td>
<td>111</td>
</tr>
</tbody>
</table>

000 = S(0)
100 = S(4)
010 = S(2)
110 = S(6)
001 = S(1)
101 = S(5)
011 = S(3)
111 = S(7)
the preceding method is to be used the imaginary part of the
S(j)'s must be set equal to zero. This represents a waste of
storage locations and a waste of computer time which can be
significant if a minicomputer is being used to perform the FFT.
By adapting the method to take into account that the S(j)'s are
real, however, it is possible to reduce the storage locations to
N/2 complex numbers and halve the computer time.

To accomplish this, we assume that the S(j)'s are real
and again split the S(j)'s into two sets corresponding to the
even and odd indices of S(j). Now we construct a function $T(j')$
declared as

$$T(j') = Y(j') + iZ(j') \quad \text{for } j' = 0, 1, 2, \ldots, (N/2)-1$$

(4.6-11)

If the binary bit inversion procedure is applied to the $T(j')$s,
the FFT will yield an ordered set of $E(k)$.

$$E(k) = \text{DFT}[T(j')] = \sum_{j'=0}^{N/2-1} T(j') \exp(-i2\pi j'k/[N/2])$$

(4.6-12)

We also define

$$C(k) = \text{DFT}[Y(j')] = \sum_{j'=0}^{N/2-1} Y(j') \exp(-i2\pi j'k/[N/2])$$

(4.6-13a)

and

$$D(k) = \text{DFT}[Z(j')] = \sum_{j'=0}^{(N/2)-1} Z(j') \exp(i2\pi j'k/[N/2])$$

(4.6-13b)

Using the preceding definitions, $B(k)$ can now be written as

$$B(k) = C(k) + D(k) \exp(-i2\pi k/N)$$

(4.6-14)
and
\[ B(k+N/2) = C(k) - D(k) \exp(-i2\pi k/N) \]  \hfill (4.6-15)
for \( 0 \leq k < N/2 \).

For a double sided interferogram \( B(k) \) is then calculated from
\[ [B(k)]^2 = [\text{Re } B(k)]^2 + [\text{Im } B(k)]^2 \]  \hfill (4.6-16)

The preceding method may be summarized as follows.

\( E(k) \) is obtained from the DFT of the constructed function \( T(j') \) by using the FFT. \( C(k) \) and \( D(k) \) are then obtained from these \( E(k) \). Finally, the values of \( B(k) \) are calculated from the resulting \( C(k) \) and \( D(k) \). \( C(k) \) and \( D(k) \) are calculated in terms of \( E(k) \) rather than directly from their respective DFTs. This saves computer time since no DFT except \( E(k) \) need be directly calculated.

The just described base "2" Cooley-Tukey FFT algorithm is also referred to as an "in place" and "decimation in time" (DIT) method. "In place" because each sequence of computations is stored in the original data storage locations. "Decimation in time" refers to the process of decomposing the sequence \( S(j) \) into smaller subsequences where the index \( j \) is often associated with time.

There are, however, as discussed below, many different algorithms available for performing an FFT besides the base "2" Cooley-Tukey algorithm. These algorithms were developed to overcome the restriction of the base "2" algorithm which requires that the number of data points be an integer power of two. Thus, there are base "3", "4", "8", "16", and base "4 + 2" algorithms.
There are also algorithms available for the case where the
number of data points can be expressed as a product of m integer
factors as well as an algorithm for an arbitrary number of data
points. There are also variations of these algorithms developed
by the introduction of "twiddle factors", also called phase or
rotation factors. These give rise to so-called "twiddle factor"
algorithms which reduce the number of multiplications by
exploiting the symmetries of the sine and cosine functions.

Furthermore, all these various algorithms may be
decimation in time or "decimation in frequency" (DIF) methods.
The decimation in frequency methods are usually called Sande-
Tukey algorithms (11) and will be described later. Decimation
in time methods are usually referred to as Cooley-Tukey algorithms
even though the first Cooley-Tukey algorithm was a base 2 algo-

To illustrate the conceptual developments of these
various algorithms, Equation (4.6-3) is rewritten as

$$B(k) = \sum_{j=0}^{N-1} S_0(j)W^{jk}$$

(4.6-17)

where

$$W = \exp(-i2\pi/N)$$

(4.6-18)

Now, assume that the number of data points can be expressed as
$$N = r_1r_2$$, where $$r_1$$ and $$r_2$$ are integers. The indices $$j$$ and $$k$$
are then expressed as

$$j = j_1r_2 + j_0 \quad j_0 = 0,1,\ldots,r_2 - 1 \quad j_1 = 0,1,\ldots,r_1 - 1$$

(4.6-19a)

$$k = k_1r_1 + k_0 \quad k_0 = 0,1,\ldots,r_1 - 1 \quad k_1 = 0,1,\ldots,r_2 - 1$$

(4.6-19b)
The Cooley-Tukey FFT algorithms can now be generated by writing the product $jk$ as

$$jk = kj_1r_2 + kj_0$$  \hspace{1cm} (4.6-20)

Substituting in Equation (4.6-17) yields

$$B(k_1, k_0) = \sum_{j_1=0}^{r_2-1} \sum_{j_0=0}^{r_1-1} S_0(j_0, j_1)W^{k_0j_1r_2}W^0 \sum_{j_1=0}^{r_2-1} S_0(j_0, j_1)W^{k_1r_1+k_0}j_0$$  \hspace{1cm} (4.6-21)

The notation can be simplified by defining

$$r_2^{-1}$$

$$S_1(j_0, k_0) = \sum_{j_1=0}^{r_2-1} S_0(j_0, j_1)W^{k_0j_1r_2}$$  \hspace{1cm} (4.6-22a)

and

$$r_1^{-1}$$

$$S_2(k_1, k_0) = \sum_{j_0=0}^{r_1-1} S_1(j_0, k_0)W^{k_1r_1+k_0}j_0$$  \hspace{1cm} (4.6-22b)

and

$$B(k_1, k_0) = S_2(k_1, k_0)$$  \hspace{1cm} (4.6-22c)

The input data array $S_0(j_0, j_1)$ is in bit inverted order so that the output array $S_2(k_1, k_0)$ is in order. If the input data array is in order, then the output array would be in bit inverted order. If $N = 4r_2$, then these relationships would define the base 4 algorithm; if $N = 8r_2$, the base 8 algorithm, etc.

The Sande-Tukey FFT algorithms can be generated by writing the product $jk$ as

$$jk = j(k_1r_1 + k_0)$$  \hspace{1cm} (4.6-23)

where $j$ and $k$ are defined by Equations (4.6-19). Substitution of this $jk$ into Equation (4.6-17) yields
\[
B(k_1, k_0) = \sum_{j_0=0}^{r_1-1} \left[ \sum_{j_1=0}^{r_2-1} S_0(j_0, j_1) W^{(j_1 r_2 + j_0)r_1} \right] W^{-j_0 r_1 r_1} \quad (4.6-24)
\]

The notation can again be simplified by defining
\[
S_1(j_0, k_0) = \sum_{j_1=0}^{r_2-1} S_0(j_0, j_1) W^{k_0 j_1 r_2 + k_0 j_0} \quad (4.2-25a)
\]
and
\[
S_2(k_1, k_0) = \sum_{j_0=0}^{r_1-1} S_1(j_0, k_0) W^{j_0 r_1 r_1} \quad (4.6-25b)
\]
and
\[
B(k_1, k_0) = S_2(k_1, k_0) \quad (4.6-25c)
\]

A comparison of Equations (4.6-20, 21, 22) to Equations (4.6-23, 24, 25) shows that, in this case, the components of \( k \) are separated instead of the components of \( j \). This particular process of decomposing the DFT of \( B(k) \) with respect to the index \( k \) is called "decimation in frequency" since the index \( k \) is generally associated with frequency. As with the Cooley-Tukey FFT algorithms, different bases may also be implemented with the Sande-Tukey FFT algorithms.

The just described Cooley-Tukey and Sande-Tukey FFT algorithms may be made more efficient by exploiting the symmetries of the sine and cosine functions. This can be accomplished by re-grouping the factors of \( W \) in their respective equations. As a result of this re-grouping, "twiddle factors" are introduced giving rise to "twiddle factor" FFT algorithms. The development of these algorithms can be illustrated through the use of the
Cooley-Tukey FFT algorithms. For instance, with a re-grouping of the factors of $W$, Equation (4.6-21) can be rewritten as

$$B(k_1, k_0) = \sum_{j_0=0}^{r_2-1} \left[ \sum_{j_1=0}^{r_1-1} S_0(j_0, j_1) W^{k_0j_1r_2} \right] W^{k_0j_0r_1} \quad (4.6-26)$$

Equations (4.6-22) can now be expressed as

$$S_1(j_0, k_0) = \left[ \sum_{j_1=0}^{r_1-1} S_0(j_0, j_1) W^{k_0j_1N/r_1} \right] W^{k_0j_0} \quad (4.6-27a)$$

and

$$S_2(k_1, k_0) = \sum_{j_0=0}^{r_2-1} S_1(j_0, k_0) W^{k_1j_0r_1} \quad (4.6-27b)$$

and

$$B(k_1, k_0) = S_2(k_1, k_0). \quad (4.6-27c)$$

The factor $W^{k_0j_1N/r_1}$ takes on discrete values only, depending upon the values of $j_0, j_1$. As a result, the transform in brackets for $S_1(j_0, k_0)$ can be evaluated without multiplications. These results are then referenced or "twiddled" by the factor $W^{k_0j_0}$ outside the brackets.

As an illustration, consider the example of a 16 point base 4 transform. In this case $r_1 = r_2 = 4$ and $j$ and $k$ range from 0 to 3. The factor $W^{k_0j_1N/r_1}$ becomes $W^{k_0j_1}$ and can only have the values $\pm 1$ and $\pm i$. Thus, the 4-point transform in brackets for $S_1(j_0, k_0)$ can be evaluated without any multiplication. Thus, the number of multiplications are reduced by exploiting the symmetries of the sine and cosine functions.

In an analogous manner, the case for $N = r_1r_2 \ldots, r_m$,
where $r_1, r_2, \ldots, r_m$ are integers, can also be developed. With this situation the indices $j$ and $k$ are represented as

$$
j = j_{m-1}(r_2 r_3 \ldots r_m) + \cdots + j_1 r_1 + j_0 \tag{4.6-28a}
$$

$$
k = k_{m-1}(r_1 r_2 \ldots r_m-1) + \cdots + k_1 r_1 + k_0 \tag{4.6-28b}
$$

where

$$
j_i = 0, 1, 2, \ldots, r_{m-i} - 1 \quad 0 \leq i \leq m-1 \tag{4.6-29a}
$$

$$
k_{i-1} = 0, 1, 2, \ldots, r_i - 1 \quad 1 \leq i \leq m \tag{4.6-29b}
$$

Equation (4.6-17) can now be rewritten in terms of this representation and evaluated in a manner similar to the case of $N = r_1 r_2$.

For the case of arbitrary $N$, an algorithm developed by Bluestein (12) can be used. With this algorithm, the product $jk$ is written as

$$
jk = jk + (j^2 - j^2 + k^2 - k^2)/2 \tag{4.6-30}
$$

Letting

$$
y(j) = W^j \tag{4.6-31}
$$

and

$$
h(k - j) = W^{-(k-j)^2/2} \tag{4.6-32}
$$

Equation (4.6-17) can be written as

$$
B(k) = W^{k^2/2} \sum_{j=0}^{N-1} y(j) h(k-j) \tag{4.6-33}
$$

This equation is now in the form of a convolution. The functions $y(j)$ and $h(j)$ are augmented with sufficient zeros so that they are of length $N'$ before the equation is evaluated. If $N'$ is
about 64 or greater, using the FFT approach to compute Equation (4.6-33) requires less computer time than computing Equation (4.6-33) directly (13). Using this procedure the FFT for any value of N can be evaluated by multiplying the result of the convolution by the factor $w_k^2/2$.

As can be seen, there are many variations of the FFT algorithm. Each version has been developed to utilize the particular properties of the data being analysed, of the computer involved, or of the special-purpose FFT hardware available. The advantages of using a higher base number algorithm is that it reduces the total required multiplications. The disadvantage is that it requires more involved operations. However, the majority of these algorithms are founded on the Cooley-Tukey algorithm or the Sande-Tukey algorithm.

The off-line computer program used in the present work utilizes the base 2 Cooley-Tukey FFT algorithm. It is given in Appendix B. The essence of the program was adapted from Appendix B of reference (9) with major modifications made to suit our particular needs. The bit inversion routine was adapted from reference (14) as it was deemed simpler.

The modifications made for our system include the routines for entering and calculating input parameters, the data collection routine, the plotting routine, provisions for obtaining averaged background and sample spectra, and provisions for recording the spectra on disc. Further, we developed facilities such that ratioed spectra may also be calculated and plotted. Original spectra stored in files on disc may also be recalled and re-
plotted if desired.

There are two data collection routines available in our program. One routine is for normal data collection. The other routine was devised to try and extend the wavenumber limit of the interferometer to twice its maximum of 625 per cm. (Since the smallest available path difference is 8 microns, the shortest non-aliased wavelength is 16 microns. This corresponds to a maximum of 625 per cm.) It does this by always splitting in half the time required to scan the last 8 microns. In effect, the routine tries to simulate a path difference of 4 microns, thus doubling the maximum range. However, even though filter and beam splitter restrictions could be accommodated to extend the range, the variation in the speed of the mirror drive was too great between sampling points to produce a reliable and repeatable spectrum. For the present, this data gathering routine is not used but is left as part of the program for possible future use with an improved mechanical system.

IV.7 Experimental Set-up

The experimental block diagram of our set-up to obtain far infrared spectra is shown in Figure 4.11. The output of the Golay detector, which is an integral part of the interferometer, is fed to a lock-in amplifier. The chopper frequency is input to the lock-in amplifier as the reference frequency. The analog output of the lock-in amplifier is then used as a differential input to the analog to digital converter (A/D) rather than as a single-ended input. With a single-ended input, the
Fig. 4.11 Block Diagram of Far-Infrared System.
desired input signal to the A/D is referenced to the source ground at the source and to the computer ground at the A/D. As such, any potential difference between source and computer grounds appears as an additional and undesirable input to the A/D. With a differential input, the source signal and ground lines are both connected as inputs to the A/D. As such, any ground loop noise appears on both lines as an input to the A/D. However, the output of the A/D is taken as a function of the instantaneous difference between the voltages on the two lines. Thus, a differential input eliminates ground loop noise whereas a single-ended input does not.

Within the interferometer is a set of Moiré gratings. One grating is attached to the movable mirror while the other remains stationary. A light and photocell assembly is situated such that for every eight microns of path difference a pulse is output. These Moiré pulses are then amplified and square-wave shaped for input to a path difference selector.

The path difference selector has provisions for selecting a path difference of 8, 16, 32, or 64 microns, depending upon the maximum wavenumber desired. It does this by means of flip-flop counters which allow every Moiré pulse, every other Moiré pulse, every fourth Moiré pulse, or every eighth Moiré pulse to be output. These square-wave outputs are then converted to 2 micro-second trigger pulses for input to the A/D converter via a Schmitt trigger. The short duration of the trigger pulses permits firing the Schmitt trigger on either the positive or negative
slope of a trigger pulse. The steepness of the slopes ensures that the difference in time is negligible between the actual and selected firing points.

The A/D converter is designated as ADV11-A by the Digital Equipment Corporation and is, physically, part of the PDP-11 minicomputer used in this work, also supplied by the Digital Equipment Corporation. The A/D converter is fully programmable and has provisions for initiating conversions by program control, a realtime clock, or by external triggers. The Moire pulses were used in this instance as external triggers to initiate the A/D conversions of the analog input signal from the lock-in amplifier. The resulting digital data was then input to the computer.

The computer under control of the program, in Appendix B, outputs instructions to the operator as to where to start the interferometer and which path difference to select. It then collects the digital data from the A/D converter, performs the FFT, plots the spectrum on the CRT terminal and stores the spectrum on disc.

The interferometer is a Beckman Instruments Model IR720 Fourier Spectrophotometer designed for use in the 10-500 per cm region. It consists of a series of 6 modules bolted together and is depicted in Figure 4.12. The modules comprising the interferometer are designated as the source module, beam splitter module, drive module, condenser module, sample chamber module, and detector module.

The source module houses the source, chopper, and an off-axis paraboloid mirror. The source is a 90 watt, high
Fig. 4.12 FS-720 Far-Infrared Spectrometer.
pressure, water-cooled mercury vapor lamp enclosed in a quartz envelope. A 3, 5, or 10 mm diameter source aperture can be selected. The chopper is synchronously driven at 15 Hertz and has provisions for providing this frequency as the reference for a lock-in amplifier. The off-axis paraboloid is a three inch diameter surface aluminized mirror having a focal length of 115 mm. The mirror collimates and directs the radiation to the beam splitter module.

The beam splitter module consists of the beam splitter and the fixed mirror of the Michelson interferometer. The beam splitter rests in a mount made of spot-ground stainless steel. The mount is constructed such that the beam splitter can be easily replaced without the need for realignment. The beam splitter itself can be any one of five different thicknesses of Mylar (polyethylene terephthalate) depending upon the maximum wavenumber desired. The thicknesses range from 15 gauge (3.5 microns) to 200 gauge (50 microns) in steps of two. The fixed mirror is a three inch diameter surface aluminized plane mirror with provisions for adjustment.

The drive module houses the movable mirror of the Michelson interferometer, the Moire gratings, the speed and drive motors, and the lamp and photocells to provide the Moire pulses. The movable mirror is identical to the fixed mirror and can be driven a maximum path difference of ± 10 cm providing for resolutions of up to 0.1 per cm. The speed motor is capable of selecting various gear ratios giving path difference speeds of
from 0.5 microns per second to 500 microns per second. The Moire gratings, light, and photocells provide for accurate determination of mirror displacement.

The condenser module consists of a surface aluminized off-axis paraboloid and plane mirror to form an image of the source in the center of the sample chamber.

The sample chamber module contains the sample holder, filters, and various mirrors. The sample holder can accommodate up to five samples, any one of which can be rotated into position by an external control. The filters are incorporated on a six position filter wheel which can also be externally controlled. One position of the filter wheel blanks the beam. The various mirrors are all surface aluminized and are used to focus and reflect the beam from the condenser module to the detector module. The final plane mirror, nearest the detector unit, can be turned through ninety degrees to permit transmittance or reflectance studies.

The detector module includes the detector and light cone. The detector is a Golay detector with a 3 mm diamond window which receives the energy transferred by the electro-formed copper light cone.

The entire instrument can be evacuated or kept filled with a dry inert gas to eliminate atmospheric water vapor absorption and is capable of holding a pressure of below 0.1 mm of mercury. The sample chamber is isolated from the rest of the system by a vacuum tight window and incorporates its own
evacuation fittings.

As mentioned earlier, there are a variety of beam splitters available. The necessity of using different beam splitters arises from the interference effects produced by the reflection of the beam from the outside and inside surfaces of the beam splitter. The path difference between rays reflected from these surfaces is

$$\delta = 2nt \cos \theta$$

where \( n \) is the index of refraction of the beam splitter, \( t \) is the thickness of the beam splitter, and \( \theta \) is the angle of refraction. Assuming that the rays strike the beam splitter at an incident angle of 45 degrees, the use of Snell's law and the condition for destructive interference gives

$$\frac{1}{\lambda} = \sigma = \frac{m}{\sqrt{2} t (2n^2 - 1)^{\frac{1}{2}}}$$

The last equation gives the wavenumbers at which minima will occur for various thicknesses of the beam splitter, knowing the index of refraction of the beam splitter. Letting \( m \) equal one and taking \( n \) to be approximately 1.8 for Mylar, the wave numbers at which the first minima occur for various thicknesses of beam splitters may be obtained. This is shown in Table IV-2 along with the wavenumbers for the first maximum. It may also be shown that the maxima occur midway between the minima. Figure 4.13 is a plot of beam splitter efficiencies for various thicknesses of beam splitters versus wavenumber. This shows quite clearly why the beam splitter must be properly matched to the
Fig. 4.13  RELATIVE BEAM SPLITTER EFFICIENCIES

TABLE IV-2
Beam Splitter Data

<table>
<thead>
<tr>
<th>Thickness (microns)</th>
<th>1st Maximum (per cm)</th>
<th>1st Minimum (per cm)</th>
<th>Approximate Range (per cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>432</td>
<td>863</td>
<td>80 - 780</td>
</tr>
<tr>
<td>6</td>
<td>252</td>
<td>503</td>
<td>40 - 460</td>
</tr>
<tr>
<td>12</td>
<td>126</td>
<td>252</td>
<td>20 - 230</td>
</tr>
<tr>
<td>25</td>
<td>63</td>
<td>126</td>
<td>10 - 115</td>
</tr>
<tr>
<td>50</td>
<td>31</td>
<td>63</td>
<td>5 - 58</td>
</tr>
</tbody>
</table>

wavenumber region of interest to avoid these interference effects.

The filters previously mentioned in the sample chamber are used to prevent aliasing. The filter to be used is selected according to the maximum wavenumber desired in the spectrum. The effects of our four available filters are shown in Figure 4.14. The figures represent the effects of the different filters on a normalized spectrum obtained under vacuum with no samples present. A 15 gauge beam splitter was used and the maximum wavenumber was 625 per cm. Since the spectral intensity distribution of the source is fairly constant in this range, the figures are actual representations of the allowed frequencies passed by the different filters.
Fig. 4.14(a) Filter #1 transmission characteristics.
Fig. 4.14(b) Filter #2 transmission characteristics.
Fig. 4.14(c) Filter #3 transmission characteristics.
Fig. 4.14(d) Filter #4 transmission characteristics.
CHAPTER V

INFRARED RESULTS
V.1 Introduction

Only room temperature far-infrared spectra were obtained in the present work. The crystals used in this study consisted of nominally pure and doped samples of CaF$_2$, BaF$_2$ and SrF$_2$. Tables V-1, 2 and 3 list the dopants, concentrations and thicknesses of these samples.

Since the local mode frequencies of interest in the present work occur between 400 cm$^{-1}$ and 500 cm$^{-1}$, the primary spectral region in the far-infrared work extended from 0 to 625 cm$^{-1}$. Spectra were also obtained in the regions of 0 to 312 cm$^{-1}$ and 0 to 156 cm$^{-1}$. The maximum frequencies in each region correspond to path difference increments of eight, sixteen, and thirty-two microns, respectively, as previously noted. However, spectra were not necessarily obtained in all three regions for all samples.

The intensity of the radiation transmitted by the samples is also very low in these regions. This is a consequence of the strong absorption and reflection of the incident radiation by the samples in these regions. As a result, the detector output has a small signal to noise (S/N) ratio. Assuming that the noise is random but the signal is not, averaging techniques may be used to eliminate the noise while enhancing the signal producing a better S/N ratio. In the present work, the spectrum for each sample was obtained a number of times. The resultant spectrum represents an average of these individual spectra. The average was obtained by adding all the individual spectra, point by point, and dividing by the number of spectra. Each spectrum presented here represents an average of
\textbf{TABLE V-1}

\textit{CaF}_2\textit{ Samples Used in Far-Infrared Studies}

<table>
<thead>
<tr>
<th>RE$^{+3}$</th>
<th>Concentration (% Atomic)</th>
<th>Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>--</td>
<td>0.50</td>
</tr>
<tr>
<td>Ce</td>
<td>0.01</td>
<td>0.52</td>
</tr>
<tr>
<td>Ce</td>
<td>0.05</td>
<td>0.52</td>
</tr>
<tr>
<td>Ce</td>
<td>0.2</td>
<td>0.51</td>
</tr>
<tr>
<td>Ce</td>
<td>0.5</td>
<td>0.80</td>
</tr>
<tr>
<td>Ce</td>
<td>1.0</td>
<td>0.64</td>
</tr>
<tr>
<td>Nd</td>
<td>0.01</td>
<td>1.28</td>
</tr>
<tr>
<td>Nd</td>
<td>0.1</td>
<td>0.60</td>
</tr>
<tr>
<td>Nd</td>
<td>1.0</td>
<td>1.30</td>
</tr>
<tr>
<td>Dy</td>
<td>0.01</td>
<td>0.66</td>
</tr>
<tr>
<td>Dy</td>
<td>0.01</td>
<td>0.86</td>
</tr>
<tr>
<td>Dy</td>
<td>0.05</td>
<td>0.50</td>
</tr>
<tr>
<td>Dy</td>
<td>1.0</td>
<td>0.63</td>
</tr>
<tr>
<td>Er</td>
<td>0.01</td>
<td>0.68</td>
</tr>
<tr>
<td>Er</td>
<td>0.05</td>
<td>0.65</td>
</tr>
<tr>
<td>Er</td>
<td>0.5</td>
<td>1.05</td>
</tr>
</tbody>
</table>
### TABLE V-2
SrF$_2$ Samples Used in Far-Infrared Studies

<table>
<thead>
<tr>
<th>RE$^{+3}$</th>
<th>Concentration (% Atomic)</th>
<th>Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>--</td>
<td>0.60</td>
</tr>
<tr>
<td>Nd</td>
<td>0.005</td>
<td>1.12</td>
</tr>
<tr>
<td>Nd</td>
<td>0.05</td>
<td>0.63</td>
</tr>
<tr>
<td>Dy</td>
<td>0.1</td>
<td>0.55</td>
</tr>
</tbody>
</table>

### TABLE V-3
BaF$_2$ Samples Used in Far-Infrared Studies

<table>
<thead>
<tr>
<th>RE$^{+3}$</th>
<th>Concentration (% Atomic)</th>
<th>Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>--</td>
<td>0.60</td>
</tr>
<tr>
<td>--</td>
<td>--</td>
<td>0.78</td>
</tr>
<tr>
<td>Ce</td>
<td>0.01</td>
<td>0.40</td>
</tr>
<tr>
<td>Ce</td>
<td>0.05</td>
<td>0.72</td>
</tr>
<tr>
<td>Pr</td>
<td>0.01</td>
<td>0.65</td>
</tr>
<tr>
<td>Pr</td>
<td>0.05</td>
<td>0.55</td>
</tr>
<tr>
<td>Nd</td>
<td>0.01</td>
<td>0.75</td>
</tr>
<tr>
<td>Nd</td>
<td>0.05</td>
<td>0.85</td>
</tr>
<tr>
<td>Dy</td>
<td>0.05</td>
<td>0.82</td>
</tr>
<tr>
<td>Dy</td>
<td>0.1</td>
<td>0.89</td>
</tr>
<tr>
<td>Er</td>
<td>0.05</td>
<td>0.92</td>
</tr>
</tbody>
</table>
about twenty runs.

V.2 Types of Spectra

There were five types of spectra obtained with the samples: transmission, transmission ratioed, reflection, reflection ratioed, and absorption coefficient. Each type of spectrum, however, was not obtained for all samples. Samples for which transmission spectra were obtained were also used to generate transmission ratioed spectra. Similarly, reflection ratios were obtained for those samples in which reflection spectra were obtained.

Transmission spectra were obtained for all hosts and doped samples of CaF$_2$, SrF$_2$, and BaF$_2$. Transmission spectra for CaF$_2$ samples, however, were not obtained in the region from 0 to 625 cm$^{-1}$ while only CaF$_2$:Dy samples provided transmission spectra in the 0 to 156 cm$^{-1}$ region. Transmission spectra for SrF$_2$ samples were only obtained in the 0 to 625 cm$^{-1}$ region while for BaF$_2$ samples they were not obtained in the region from 0 to 312 cm$^{-1}$.

Ratios of transmission spectra were generated to remove the effects of the background. The background being either a no sample (vacuum) spectrum or a host transmission spectrum. Thus, three types of these transmission ratioed spectra were produced. One type was produced by dividing the transmission spectra of the doped samples by the transmission spectrum of the appropriate host crystal. These ratioed spectra then represent the absorption spectra of the corresponding RE$^{+3}$ dopant only. The other types of ratioed spectra were obtained by dividing the transmission spectra of either the doped samples or the host crystals by the vacuum spectrum. These
resultant ratioed spectra represent the absorption spectra of the corresponding samples.

Reflection spectra were not obtained for SrF$_2$ samples while only reflection spectra for BaF$_2$:Pr$^{3+}$ in the 0 to 625 cm$^{-1}$ region were obtained. Reflection spectra for CaF$_2$:Dy samples were obtained in the 0 to 156 cm$^{-1}$ region and for CaF$_2$:Er samples in the 0 to 312 cm$^{-1}$ region.

Reflection ratioed spectra were produced by dividing the reflection spectra of the doped samples by the reflection spectrum of the appropriate host crystal. This was done to try to determine what effect the dopant would have on the reflectivity of the sample. A decrease in the reflectivity of a doped sample compared to the host crystal would mean an absorption of radiation due to the dopant, providing the initial intensities of radiation were the same for host and sample. An absorption at the frequency of a "local mode" would indicate that, perhaps, the "local mode" may really be a crystal mode. Absorption would imply propagation of the frequency by the crystal which constitutes a crystal mode, not a local mode. Similarly, no decrease in reflectivity would tend to support the view that these modes are actually local modes.

Absorption coefficient spectra ($k$ vs $\sigma$) were generated for CaF$_2$ only. The absorption coefficient was calculated point by point, using the expression,

$$ k(\sigma) = -\frac{1}{t} \ln \frac{I(\sigma)}{I_0(\sigma)} $$

where $t$ was the thickness of the sample in cm. The ratio of $I/I_0$ represents the absorption spectrum of a sample, a host crystal or dopant depending upon which absorption coefficient spectrum was to be generated.

V.3 Vacuum Spectra

No sample (vacuum) spectra were obtained in each of the three regions for each of the four filters (Fig. 4.4).
filters are numbered according to their positions on a six position filter wheel. Filter #5 is totally absorbing from 0 to 625 cm\(^{-1}\). There is no filter in the sixth position of the wheel. The purpose of this position is to blank the beam to the detector. There were two uses for the vacuum spectra. One use was to generate transmission ratioed spectra as described above. The other use was to determine the bandpass of each of the four filters. This was necessary because no bandpass information for any filter was supplied by the manufacturer of the interferometer. The vacuum spectra represents the actual bandpass of each filter since the output of the source is fairly constant from about 10 cm\(^{-1}\) to 625 cm\(^{-1}\) (Fig. 4.2). The vacuum spectra shows that filters #1 and #4 should be used in the 0 to 156 cm\(^{-1}\) region. Filter #3 is used from 0 to 312 cm\(^{-1}\) and filter #2 is to be used in the region from 0 to 625 cm\(^{-1}\).

V.4 General Spectral Observations (Figs. 5.1-5.32)

A detailed study of the spectra reveals that there are many similarities among them. Spectra of samples with the same host crystal are quite similar. Spectra of samples with different host crystals show that they possess the same general features but these features are shifted in wavenumber from host to host.

Transmission spectra of BaF\(_2\):RE\(^{+3}\) samples and the BaF\(_2\) host crystal show three broad bands in the region from 0 to 625 cm\(^{-1}\). The first band extends from about 10 cm\(^{-1}\) to about 150 cm\(^{-1}\) with
the peak at approximately 60 cm\(^{-1}\). The second band is approximately 90 cm\(^{-1}\) wide and extends from about 460 cm\(^{-1}\) to about 550 cm\(^{-1}\). This band has a fairly flat peak between about 490 cm\(^{-1}\) to 520 cm\(^{-1}\). The third band is characterized by a continuous increase in transmission from about 550 cm\(^{-1}\) to a peak at about 605 cm\(^{-1}\). A very slight decrease in transmission occurs after the peak with a minimum at 615 cm\(^{-1}\) followed by an increase in transmission to 625 cm\(^{-1}\), the limit of measurability of the instrument. The relative amplitudes of the three peaks varies with the thickness of the samples. As the thickness decreases the amplitude of the second peak approaches that of the first peak. The amplitude of the third peak, in the majority of spectra, is greater than either the first or second peak. The spectrum of Ba\(_2\)F\(_2\):Ce\(^{3+}\) of thickness 0.40 mm shows about 50\% relative transmission for the first and second peak while the third peak is at \(\%\) 100\% relative transmission. The minimum between the second and third peak in this spectrum is at about the 10\% relative transmission level. This minimum is about the 0\% transmission level for the other spectra.

The absorption spectra of the Ba\(_2\)F\(_2\) samples (Ba\(_2\)F\(_2\):RE\(^{3+}\)/VAC) and host (Ba\(_2\)F\(_2\)/VAC) reveals the same three peaks. The amplitudes of these peaks are greatly reduced, however, indicating very little sample and host transmission throughout the region from 0 to 625 cm\(^{-1}\). The absorption spectrum of the Ba\(_2\)F\(_2\):Ce\(^{3+}\) sample mentioned above shows the peak of the first band at the 93\% absorption level. The second peak is at the 96\% absorption level while the third peak shows 82\% absorption. The rest of the spectrum indicates 100\% absorption.
All other absorption spectra of BaF$_2$ samples and host show the same results but less pronounced. The absorption spectra of the RE$^{+3}$ dopants (BaF$_2$:RE$^{+3}$/BaF$_2$) are extremely noisy. Any absorption due to the RE$^{+3}$ impurities cannot be reliably determined for any of these spectra.

The reflection spectra of the BaF$_2$ samples, including the host, shows a broad reflection band extending from approximately 180 cm$^{-1}$ to 315 cm$^{-1}$ at the 50% relative reflection levels with a peak at about 240 cm$^{-1}$ indicating 100% relative reflection. The band shows a gradual increase in relative reflection from 0 to 180 cm$^{-1}$ and a fairly rapid decrease in reflection past 315 cm$^{-1}$. The relative reflection is about 0% from 375 cm$^{-1}$ to 625 cm$^{-1}$.

The reflection ratioed spectra of the BaF$_2$ samples show a fairly constant ratio in regions of relatively high reflection (180 cm$^{-1}$ to 315 cm$^{-1}$). The other regions of the spectra, however, are extremely noisy. No effect due to the RE$^{+3}$ impurities could be detected in the 180 cm$^{-1}$ to 315 cm$^{-1}$ region nor reliably determined elsewhere.

Transmission and absorption spectra of SrF$_2$ samples are, qualitatively, the same as for BaF$_2$ samples. The corresponding spectra of the first bands are nearly identical except the extent of the first band is about from 10 cm$^{-1}$ to 135 cm$^{-1}$. The corresponding spectra of the second bands are also the same except the second band extends from about 550 cm$^{-1}$ to 625 cm$^{-1}$ for SrF$_2$ samples. The third band is not present in these spectra. Absorption spectra are too noisy to reliably determine any absorption due to the RE$^{+3}$
impurities.

Transmission spectra of CaF$_2$ samples reveal the presence of only the first band in the corresponding spectra of BaF$_2$ and SrF$_2$ samples. The spectra also show 0% relative transmission from about 312 cm$^{-1}$ to 625 cm$^{-1}$. Therefore, only the 0 to 156 cm$^{-1}$ and 0 to 312 cm$^{-1}$ regions were utilized for spectra. The transmission band that appears in these spectra is identical to the first bands in the transmission spectra of BaF$_2$ and SrF$_2$ samples except it extends from 10 cm$^{-1}$ to 105 cm$^{-1}$. Absorption spectra were considered too noisy to provide any meaningful results.

Reflection spectra of CaF$_2$ samples show a broad reflection band extending from about 55 cm$^{-1}$ to 200 cm$^{-1}$ at the 50% relative reflection points with 100% relative reflection at about 125 cm$^{-1}$. Reflection ratioed spectra show a fairly constant ratio in the regions of relatively high reflection. No effects due to the RE$^{+3}$ impurities could be determined from these ratios.

The absorption coefficient spectra of the CaF$_2$ samples are only useful in the region of the transmission bands of the corresponding transmission ratioed spectra. This is only valid, however, if the intensity of the transmitted radiation through the samples is sufficient to produce a meaningful ratio. The regions outside of the transmission bands of the transmission ratioed spectra show 0% transmission (100% absorption) and k values obtained in these regions are, therefore, doubtful. The absorption coefficient spectra show a steady increase in k values from a minimum at about a frequency of 25 cm$^{-1}$. The minimum value of k at this frequency
ranges from 15 cm\(^{-1}\) to 20 cm\(^{-1}\) in these spectra. There is a
great variation in the maximum value of \(k\) from spectrum to spectrum.
The maximum values of \(k\) occur in regions of the spectra which
show 0% transmission.
Fig. 5.1  Nominally pure CaF$_2$ RT transmission spectrum. 0.50 mm thick.
Fig. 5.2  Nominally pure CaF$_2$ RT transmittance.
0.50 mm thick.
Fig. 5.3  \( \text{CaF}_2: \text{Ce}^{+3} \) RT transmission spectrum.

0.05% concentration - 0.52 mm thick.
Fig. 5.4 CaF$_2$:Nd$^{+3}$ RT transmission spectrum.  
0.1% concentration - 0.60 mm thick.
Fig. 5.5  \( \text{CaF}_2 : \text{Nd}^{3+}/\text{CaF}_2 \) RT absorption spectrum.

\( \text{CaF}_2 : \text{Nd}^{3+} \) - 0.1% concentration - 0.60 mm thick.

\( \text{CaF}_2 \) - 0.50 mm thick.
Fig. 5.6 \( \text{CaF}_2: \text{Er}^{3+} \) RT transmittance.

0.60 mm thick.
Fig. 5.7  Nominaly pure CaF$_2$ RT reflection spectrum.
Fig. 5.8 \textit{CaF}_2:Ce^{+3} \text{ RT reflection spectrum.}

0.05\% concentration.
CaF$_2$:Ce$^{3+}$/CaF$_2$

Fig. 5.9 CaF$_2$:Ce$^{3+}$ RT reflectance
0.05% concentration.
Fig. 5.10. $\text{CaF}_2\text{:Nd}^{3+}$ RT reflection spectrum.

0.01% concentration.
Fig. 5.11  CaF$_2$:Nd$^{+3}$ RT reflectance.

0.1% concentration.

CaF$_2$:Nd$^{+3}$/CaF$_2$
Fig. 5.12 Nominally pure CaF₂ RT absorption coefficient spectrum. 0.50 mm thick.
Fig. 5.13 $\text{CaF}_2: \text{Dy}^{3+}$/VAC RT absorption coefficient spectrum. 0.63 mm thick.
Fig. 5.14  CaF₂:Er³⁺ RT absorption coefficient spectrum.

0.60 mm thick.
Fig. 5.15 Nominaly pure SrF$_2$ RT transmission spectrum.
0.50 mm thick.
Fig. 5.16 SrF₂: Nd³⁺ RT transmission spectrum.
0.05% concentration - 0.63 mm thick.
Fig. 5.17  $\text{SrF}_2: \text{Nd}^{3+}$ RT absorption spectrum.

$\text{SrF}_2: \text{Nd}^{3+}$ - 0.05% concentration - 0.63 mm thick.

$\text{SrF}_2$ - 0.50 mm thick.
Fig. 5.18  SrF$_2$:Dy$^{+3}$ RT transmission spectrum.

0.1% concentration - 0.55 mm thick.
SrF$_2$:Dy$^{3+}$/SrF$_2$

Fig. 5.19  SrF$_2$:Dy$^{3+}$ RT absorption spectrum.
SrF$_2$:Dy$^{3+}$ - 0.1% concentration - 0.55 mm thick.
SrF$_2$ - 0.50 mm thick.
Fig. 5.20  Nominal pure BaF$_2$ RE transmission spectrum.

0.60 mm thick.
Fig. 5.21  Nominal purity BaF$_2$ RT transmittance.
0.60 mm thick.
Fig. 5.22: $\text{BaF}_2:\text{Ce}^{+3}$ RT transmission spectrum.

0.05% concentration - 0.40 mm thick.
Fig. 5.23  BaF₂:Ce³⁺ RT transmittance.
0.05% concentration - 0.40 mm thick.
Fig. 5.24  \( \text{BaF}_2:Ce^{+3} \) RT absorption spectrum.

\( \text{BaF}_2:Ce^{+3} \) - 0.05% concentration - 0.40 mm thick.

\( \text{BaF}_2 \) - 0.60 mm thick.
Fig. 5.25  BaF$_2$:Dy$^{3+}$ RT transmission spectrum.
0.05% concentration - 0.82 mm thick.
Fig. 5.26  BaF$_2$:Dy$^{3+}$/VAC RT transmittance.

- 0.05% concentration - 0.82 mm thick.
Fig. 5.27  $\text{BaF}_2: \text{Dy}^{3+}$ RT absorption spectrum.

$\text{BaF}_2: \text{Dy}^{3+}$ - 0.05% concentration - 0.82 mm thick.

$\text{BaF}_2$ - 0.78 mm thick.
Fig. 5.28  Nominally pure $\text{BaF}_2$ RT reflection spectrum.
Fig. 5.29  BaF$_2$:Pr$^{3+}$ RT reflection spectrum.
0.01% concentration.
Fig. 5.30  BaF$_2$:Pr$^{3+}$/BaF$_2$ RT reflectance.
0.01% concentration.
Fig. 5.32  \( \text{BaF}_2: \text{Dy}^{3+} \text{RT reflectance.} \)

0.05\% concentration.
CHAPTER VI
DISCUSSION
VI.1 Ultra-Violet Spectra

Previous work with CaF₂:RE⁺³ spectra by Kaplyanski et al. (1), Loh (2), Hayes et al. (3), Schlesinger and Szczurek (4) and others (see References 1-4 and references therein) had revealed the existence of a vibrational mode at approximately 485 cm⁻¹. The single phonon density of states curve given by Elcombe and Pryor (5) shows a maximum frequency at about 465 cm⁻¹ for pure CaF₂. Due to the small difference between these frequencies, it could not be readily established whether the 485 cm⁻¹ frequency belonged to a local vibrational mode or a crystal vibrational mode.

Hayes et al. (3) who performed work on the CaF₂:Ce⁺³ system proposed that the 485 cm⁻¹ frequency belonged to a local vibrational mode. They suggested this local mode was due to the vibration of the eight nearest neighbor fluorine ions about the Ce⁺³ ion (the so-called "breathing" mode). The increase in the frequency of this mode above the "cutoff" of lattice frequencies was assumed to be due to an increase in the force constant. They attributed the increase in the force constant to be due to the larger ionic radius of the Ce⁺³ ion (r = 1.11Å) as compared to the Ca⁺² ion (r = 0.99Å), which it replaces.

However, Schlesinger and Szczurek (6,7) had shown in their work on CaF₂:Ho⁺³, Tb⁺³, Dy⁺³ systems that the 485 cm⁻¹ frequency was independent of the rare earth dopant as well as the concentration of dopant. Two approaches were used in their work. With one approach, spectra were obtained for different concentrations of the same RE⁺³ impurity imbedded in the CaF₂ matrix. An analysis of these
spectra revealed the same 485 cm\(^{-1}\) frequency appeared in all such spectra. The second approach was to obtain CaF\(_2\):RE\(^{+3}\) spectra for which the ionic radii of the RE\(^{+3}\) impurities were greater than, comparable to, and less than the ionic radius of the Ca\(^{+2}\). Hence, they chose Ho\(^{+3}\), Tb\(^{+3}\) and Dy\(^{+3}\). An analysis of these spectra also revealed the 485 cm\(^{-1}\) frequency was present in all. Thus, they had shown that the 485 cm\(^{-1}\) frequency was independent of the ionic radius of the impurity as well as the concentration of the impurity. They proposed that the 485 cm\(^{-1}\) frequency was a crystal mode to be associated with the 465 cm\(^{-1}\) frequency of the CaF\(_2\) host crystal.

Bron and Wagner (8) had shown that impurity vibronic spectra should be slightly higher than the host frequency, in agreement with their results. Furthermore, the work done by Kaplyanskii et al. (1) on CaF\(_2\):Ce\(^{+3}\) compensated with O\(^{-2}\) ions also supported this view.

Further work, extended to SrF\(_2\) and BaF\(_2\) systems, led to a resolution of this issue. The present work is an example of such work. We find here, in harmony with others, that SrF\(_2\):RE\(^{+3}\) systems and BaF\(_2\):RE\(^{+3}\) systems also possess similar vibrational modes with frequencies of 438 cm\(^{-1}\) and 405 cm\(^{-1}\), respectively. These frequencies are considerably higher than the maximum frequencies in their corresponding density of states curves.

The single phonon density of states curve given by Elcombe (9) shows that the maximum vibrational frequency is about 380 cm\(^{-1}\) for pure SrF\(_2\). The single phonon density of states curve given by Hurrell and Minkiewicz (10) shows that the maximum vibrational
frequency is approximately 330 cm\(^{-1}\) for pure BaF\(_2\). The 438 cm\(^{-1}\) and 405 cm\(^{-1}\) frequencies are far removed from these maximum frequencies. These frequencies are, consequently, designated as belonging to local vibrational modes rather than crystal vibrational modes. These results suggest that the 485 cm\(^{-1}\) frequency of the CaF\(_2\):RE\(^{3+}\) system probably belongs to a local vibrational mode as well.

The generally accepted view now is that the 485 cm\(^{-1}\) frequency of the CaF\(_2\):RE\(^{3+}\) system belongs to a local vibrational mode \(11\). This mode is the "breathing" mode previously mentioned, as proposed by Hayes et al. \(3\). Their calculations of the increase of the force constant was, however, erroneous. Schlesinger and Szczurek \(6,7\) had shown that this mode and, hence, the force constant were independent of the radii of the RE\(^{3+}\) impurity for the CaF\(_2\) host.

The frequency of this vibrational mode is, however, related to the force constant between the RE\(^{3+}\) ions and the fluorine ions. This force constant is determined, primarily, by the size of the host crystal lattice rather than the radii of the RE\(^{3+}\) ions.
As the size of the lattice increases, the distance between the RE$^{3+}$ ion and the fluorine ions increases and, thus, the force constant decreases. As the force constant decreases, so should the frequency of the vibrational mode. Conversely, a smaller lattice is associated with a larger force constant and an increase in the frequency of the vibrational mode.

The lattice constants for CaF$_2$, SrF$_2$ and BaF$_2$ (in Å) are, respectively, 5.45; 5.86 and 6.18. The frequencies (cm$^{-1}$) of their respective "breathing" modes, based on this and previous work, are approximately 485, 438 and 405. These results support the proposition set forth above.

Tables VI-1 and VI-2 present a summary of the mean values of local mode frequencies and their number of occurrences for each rare earth dopant studied in the present work. Table VI-1 pertains to the SrF$_2$ crystal host while Table VI-2 pertains to the BaF$_2$ host. The standard deviation for each dopant as well as the mean and standard deviations of the total number of entries is also given. The data for entries followed by (LHT) were obtained from their respective LHT spectrum. All other data were obtained from LNT spectra.

There is a possibility of some error in the determination of the number of occurrences of the local modes due to incorrect wavelength designations of the peaks as previously mentioned. However, even if the number of occurrences were in error by as much as ten percent, the number of occurrences per host would still exceed one hundred. The credibility of the results for each host
### TABLE VI-1
Mean Values of Local Mode Frequencies for SrF$_2$ Host

<table>
<thead>
<tr>
<th>Dopant (% Atomic)</th>
<th>Mean (cm$^{-1}$)</th>
<th>Standard Deviation</th>
<th>Number of Occurrences</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01Ce</td>
<td>435.0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>0.005Nd</td>
<td>437.8</td>
<td>1.8</td>
<td>4</td>
</tr>
<tr>
<td>0.005Nd(LHT)</td>
<td>438.4</td>
<td>3.0</td>
<td>30</td>
</tr>
<tr>
<td>0.5Dy</td>
<td>438.3</td>
<td>1.8</td>
<td>10</td>
</tr>
<tr>
<td>0.1Dy</td>
<td>439.1</td>
<td>2.8</td>
<td>8</td>
</tr>
<tr>
<td>0.1Ho</td>
<td>437.8</td>
<td>3.3</td>
<td>23</td>
</tr>
<tr>
<td>0.1Ho(LHT)</td>
<td>437.1</td>
<td>3.8</td>
<td>22</td>
</tr>
<tr>
<td>0.05Er</td>
<td>439.8</td>
<td>1.8</td>
<td>9</td>
</tr>
<tr>
<td>0.05Er(LHT)</td>
<td>437.4</td>
<td>2.7</td>
<td>8</td>
</tr>
<tr>
<td>TOTAL</td>
<td>437.9</td>
<td>3.2</td>
<td>116</td>
</tr>
</tbody>
</table>

### TABLE VI-2
Mean Values of Local Mode Frequencies for BaF$_2$ Host

<table>
<thead>
<tr>
<th>Dopant (% Atomic)</th>
<th>Mean (cm$^{-1}$)</th>
<th>Standard Deviation</th>
<th>Number of Occurrences</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01Ce</td>
<td>402.4</td>
<td>3.1</td>
<td>7</td>
</tr>
<tr>
<td>0.05Pr</td>
<td>404.4</td>
<td>2.8</td>
<td>21</td>
</tr>
<tr>
<td>0.01Nd</td>
<td>405.3</td>
<td>3.7</td>
<td>23</td>
</tr>
<tr>
<td>0.01Nd(LHT)</td>
<td>404.6</td>
<td>3.0</td>
<td>29</td>
</tr>
<tr>
<td>0.05Dy</td>
<td>407.4</td>
<td>5.3</td>
<td>17</td>
</tr>
<tr>
<td>0.1Ho</td>
<td>407.8</td>
<td>4.1</td>
<td>16</td>
</tr>
<tr>
<td>0.05Er</td>
<td>404.9</td>
<td>3.1</td>
<td>12</td>
</tr>
<tr>
<td>0.05Er(LHT)</td>
<td>404.5</td>
<td>3.3</td>
<td>19</td>
</tr>
<tr>
<td>TOTAL</td>
<td>405.1</td>
<td>4.2</td>
<td>144</td>
</tr>
</tbody>
</table>
is supported by the consistency of the results and their standard deviations.

An analysis of the data also shows that the same local mode frequency occurs for different RE$^{+3}$ ions within the same host. Furthermore, the same frequency occurs for two different concentrations of dysprosium in the SrF$_2$ host. This seems to be in accord with the CaF$_2$:RE$^{+3}$ system where the 485 cm$^{-1}$ frequency appears with different concentrations of the same RE$^{+3}$ dopant (e.g. see Reference 7).

Many conclusions can be made from an analysis of the data: First, since many different RE$^{+3}$ dopants were used per host, it appears that the local mode frequencies are independent of the RE$^{+3}$ dopant in either the SrF$_2$ or BaF$_2$ host. Secondly, although dysprosium was the only dopant used with different concentrations, by inference from the CaF$_2$:RE$^{+3}$ data, the frequency is independent of the concentration of the same RE$^{+3}$ dopant within a given host.

As mentioned in Chapter 1.3, the type of symmetry (charge compensation) present in a given crystal depends upon many parameters, such as the initial growing conditions and subsequent heat treatment of the crystal. Due to the number of parameters which must be controlled during the growth process, it is extremely unlikely that a large crystal, as used in the present work, could be produced with only one type of charge compensation. The production of such crystals en masse is yet to be realized. Moreover, different crystal manufacturers would require different control parameters. The crystals used in the present work were supplied by Harshaw Inc. and Optovac Inc. Thus, it is reasonable to assume that more than one type of symmetry was present in the samples. However, the frequency is the same for all samples of a given host. Therefore, the frequency is independent of the symmetry. This is also supported by the work of Jacobs (12) who showed that the local mode frequency of CaF$_2$:Ce$^{+3}$ is independent of the symmetry.
VI.2 Infra-red Spectra

Three major difficulties were encountered with room temperature far-infrared spectra for ionic host crystals and doped samples in the present work. All samples exhibited either extremely high reflection or high absorption from 0 to 625 cm$^{-1}$. Furthermore, the large amplitude anharmonic temperature dependent lattice vibrations masked any local mode vibrations which may have been excited. These anharmonic vibrations also increase the extent of the absorption and reflection bands at room temperature.

High reflection occurs in the region between the transverse optical (TO) frequencies and the longitudinal optical (LO) frequencies of these crystals. In this region, the complex index of refraction is purely imaginary and wavelike solutions of Maxwell's equations do not exist within the crystals. Therefore, radiation is strongly reflected in this region. This region corresponds to the frequency gap between the TO and LO branches in the dispersion curves of the crystals and is called the Reststrahl band. Room temperature reflectance curves for CaF$_2$ and BaF$_2$ are shown in figure 6.1 while Table VI-3 shows the positions of the peaks of the Reststrahl bands and the extent of the bands for all host crystals.

Strong absorption of far-infrared radiation occurs at frequencies higher than the LO frequencies in these crystals. Figure 6.2 shows the transmittance of CaF$_2$, SrF$_2$ and BaF$_2$ crystals from 0 to 2000 cm$^{-1}$ at room temperature. The practical frequency limits for these crystals are approximately 830 cm$^{-1}$, 740 cm$^{-1}$,
Fig. 6.1 CaF$_2$ and BaF$_2$ Reflectance Curves.

Fig. 6.2 Transmittance of common optical materials in the infrared.
and 665 cm\(^{-1}\) for CaF\(_2\), SrF\(_2\) and BaF\(_2\) respectively. These transmittance curves show that all of the local mode frequencies of interest (405 cm\(^{-1}\), 438 cm\(^{-1}\) and 485 cm\(^{-1}\)) lie in the region of 0% transmittance. Furthermore, the 0% transmittance region covers the entire range from 0 to 625 cm\(^{-1}\). This is due to the fact that the transmitted radiation intensity is equal to the incident intensity minus the sum of the reflected and absorbed intensities. Since there is either high absorption or high reflection throughout the 0 to 625 cm\(^{-1}\) region at room temperature, the transmitted intensity will be extremely low.

**TABLE VI-3**

Reststrahlen Bands of Host Crystals

<table>
<thead>
<tr>
<th>Host</th>
<th>Approximate Frequency of Peak (cm(^{-1}))</th>
<th>Approximate Frequencies at 50% Reflectance (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaF(_2)</td>
<td>295</td>
<td>254 - 470</td>
</tr>
<tr>
<td>SrF(_2)</td>
<td>250</td>
<td>200 - 380</td>
</tr>
<tr>
<td>BaF(_2)</td>
<td>220</td>
<td>165 - 325</td>
</tr>
</tbody>
</table>

A comparison of the BaF\(_2\) transmittance curve and the third peak of the transmission and absorption spectra of the BaF\(_2\) samples indicates that the third peak is probably the limit of the transmittance curve at 0% transmittance. Spectra from thinner BaF\(_2\) samples seem to support this view. The absence of this peak
in the spectra of SrF$_2$ and CaF$_2$ samples can be explained by the shift of their respective transmittance limits, as given in figure 6-2 with respect to BaF$_2$ toward higher wave numbers. Neither the transmission nor absorption spectrum of any sample reveals any substantial data due to the small amount of radiation transmitted through the sample. The RE$^{+3}$ absorption spectra are also extremely noisy due to the same reason.

The peak of the reflection spectra and the 50% relative reflection levels for BaF$_2$ spectra agree remarkably well with the values for the Reststrahlen band given in Table VI-3. Thus, the reflection band present in reflection spectra of BaF$_2$ samples is its Reststrahlen band which extends from 245 cm$^{-1}$ to 470 cm$^{-1}$. However, a comparison of these reflection spectra for CaF$_2$ samples to the bandpass of filter #3 shows that the reflection spectra follow the bandpass of filter #3 on the higher wavenumber side. That is, these reflection spectra represent the lower wavenumber portion of the CaF$_2$ Reststrahlen band passed by the filter.

Due to low beamsplitter efficiency and filter bandpass characteristics, the 0 to 25 cm$^{-1}$ region of all spectra are in doubt. Since the minimum values of the absorption coefficient occur at a frequency of about 25 cm$^{-1}$ in their respective spectra, it is doubtful as to whether these values are meaningful. These spectra appear to follow the filter bandpass characteristics on the low wavenumber side.

Cooling the samples to LNT, or better yet, LHT would produce a significant change in their spectra at these temperatures.
as compared to their respective room temperature spectra. Cooling the samples would substantially reduce the large amplitude of the anharmonic vibrations. Since these vibrations are temperature dependent, their excited vibrational states would be less densely populated at low temperatures. The effect would be to decrease the width of the Reststrahlen bands as well as the width of the absorption bands. Furthermore, the non-temperature dependent vibrations (harmonic vibrations), including local mode vibrations, would be exposed due to the decrease in amplitude of the anharmonic vibrations. However, since the anharmonic vibrations are responsible for the thermal expansion of solids, cooling the samples implies a contraction of the corresponding lattices. These lattice contractions would produce an increase in the lattice force constants. As such, the TO and LO frequencies would shift toward higher frequencies as the lattices are cooled. If the Reststrahlen peaks and transmission limits change favorably then there is a good possibility that the local mode frequencies in the 400 cm$^{-1}$ to 500 cm$^{-1}$ region may be detected. The best candidates for which local modes may be detected are probably BaF$_2$ samples. This is due to the proximity of the transmittance limit to the 405 cm$^{-1}$ local mode for these samples. Similar reasoning suggests that CaF$_2$ samples would probably be the least likely candidates to use for detecting the 485 cm$^{-1}$ local modes.
CHAPTER VII
SUGGESTIONS
The ultra-violet system has been in use for a number of years and as such is well established. The techniques employed in its use have also been fairly well established. On the other hand, the far-infrared system has not been in use for such a long time. It is a fairly recent system. The suggestions presented here will, therefore, pertain only to the far-infrared system. That is not to say, however, that no suggestions could be made to improve the ultra-violet system, such as computerizing the data acquisition.

The first suggestion is to scan only a one-sided interferogram instead of a double-sided interferogram as was done in the present work. This would necessitate the computation of phase errors to correct for not sampling exactly at zero path difference. Although the computer program would have to be lengthened to accommodate this computation, the computation time required by the computer could probably be measured in milliseconds. The time required to scan a one-sided interferogram, however, is only half that required to scan a double-sided interferogram. The savings in time could be quite substantial since only half the time would be required for twenty repeated scans compared to the double-sided interferogram time requirement. The FFT algorithm could also be shortened and memory storage space would be halved. Furthermore, the one-sided interferogram has a larger S/N ratio than a two-sided interferogram which could allow fewer scans to be made.

The second suggestion is to use an oscilloscope to display the spectrum in real-time applications. The time required to plot
a spectrum of 512 points on the console CRT using the vendor supplied software routine takes about seven seconds; much too long for real-time applications. Plotting the spectrum on the oscilloscope using the D/A converter would not take as long. A further time savings could be realized by storing an arc cosine look-up table to be used by the Fourier transform routine instead of letting the computer calculate these. Assembly language programming would also allow faster scan times. However, a sampling interval of four microns or less would be needed to permit our samples to be used for real-time applications as described in the main text.

The third suggestion would be to try to extend the range of the interferogram to 1250 cm\(^{-1}\). This would require a four micron sampling interval. The four micron interval could, perhaps, be generated by a laser. If constant speed drive motors are perfected enough, the IR4MIC computer program in appendix B could be used to generate a four micron sampling interval from an actual sampling interval of eight microns. The beam splitter would also have to be replaced by a thinner one. The teflon spacer between the sample and optics compartments would have to be replaced too. This spacer not only vacuum isolates these compartments but also acts as a filter with a cut-off at about 800 cm\(^{-1}\). Other filters would also have to be used to prevent aliasing.

The final suggestion is to convert the interferometer from the far-infrared region to the visible region. This would necessitate the use of a laser for accurate determination of sampling
intervals. Changes would also be required of filters and beam-splitters as well as the source itself. The chopper, however, would not be needed while the detector could probably still be used since its range extends into the ultra-violet region of the spectrum. The detector window may have to be changed, however.
FLOW CHART FOR REAL-TIME PROGRAM

1. Initialize
   Obtain \( I(\infty) \)
   Enter Parameters
   Obtain \( S(-1), S(0), \) and \( S(1) \)
   Compute Error \( (\varepsilon) \)
   Compute \( T, T_0, \) \( \theta(j=0, k=0) \)

2. Compute \( B_0(\sigma) \)
   Compute \( \theta(j=1, k=0) \)
   Compute \( B_1(\sigma) \)
   Obtain Data
   Compute \( B_j(\sigma) \)
   Done?
   STOP

\[ Y \rightarrow N \]
THIS PROGRAM PERFORMS REAL TIME FOURIER TRANSFORMATION FOR USE
C IN FAR INFRARED SPECTROSCOPY USING A SINGLE SIDED INTERFEROGRAM
C BGS.DAT IS DATA FILE FOR BACKGROUND SPECTRUM ON RKO!
C SAM.DAT IS DATA FILE FOR SAMPLE SPECTRUM ON RKO!

DIMENSION X(3), B(512), IBUFF(512), BG(512), BUFF(512)
COMMON B, BG/SUBT/5, THETA, FJT, IBUFF, BUFF, BMAX, IRATIO
INTEGER DATA(1)
BMAX=0.00001
TPI=6.*ATAN(1.)

WRITE(7,50)

FORMAT(1X,' 1. SET UP TO RUN IAVE,’/,1X,’ 2. START INTERFEROGRAM
1 AND HIT 'RETURN' KEY')
PAUSE
FO=0.
DO 51 I=1,100
CALL INFR(DATA)
FD=FLOAT(DATA(I))
FO=FO+FD
CONTINUE
FO=FO/100.
WRITE(7,52) FO

FORMAT(1X,' IAVE=’,,F7.2)
WRITE(7,53)

FORMAT(1X,' 1. TO RE-RUN IAVE ENTER ’1’’,/1X,’ 2. TO CONTINUE
1 HIT 'RETURN' KEY')
READ(5,54) IAGAIN
FORMAT(I1)
IF(IAGAIN.EQ.1) GO TO 49
WRITE(7,67)

FORMAT(1X,' TO PLOT A RATIODED SPECTRUM ENTER ’1’’,/1X,’ TO PLOT A
1 BACKGROUND SPECTRUM HIT 'RETURN' KEY')
READ(5,54) IRATIO
IF(IRATIO.EQ.0) GO TO 1
CALL ASSIGN(10,'RKO\BGS.DAT',0,'OLD')
DEFINE FILE: 10 (512,2,0,0,0)

195
DO 600 I=1,512
READ(10,'I') BG(I)
600 CONTINUE
1 WRITE(7,2)
2 FORMAT(1X,'ENTER DDEL AS E15.9')
   READ(5,6) DDEL
   WRITE(7,3)
3 FORMAT(1X,'ENTER DSIG AS E15.9')
   READ(5,6) DSIG
   WRITE(7,4)
4 FORMAT(1X,'ENTER SIGL AS E15.9')
   READ(5,6) SIGL
   WRITE(7,5)
5 FORMAT(1X,'ENTER NPT AS I5')
   READ(5,7) NPT
   FNPT=FLOAT(NPT)
6 FORMAT(E15.9)
    WRITE(7,55)
55 FORMAT(1X,1, TO PLOT AT EVERY POINT ENTER '1'//,1X,
          2, TO PLOT ONLY AFTER COMPLETION HIT 'RETURN' KEY')
         READ(5,54) NOPLOT
         WRITE(7,60)
60 FORMAT(1X,'START INTERFEROMETER NEAR ZPD AND HIT 'RETURN' KEY')
         CALL PLOT55(2,0,2)
         CALL PLOT55(2,512,0)
         CALL PLOT55(1,0,0)
         CALL PLOT55(2,1+2+32+64,0)
         CALL PLOT55(7,0,0)
         CALL PLOT55(9,0,0)
         CALL PLOT55(10,0,0)
         CALL PLOT55(9,0,23)
         CALL PLOT55(4,1,0)
DO 500 I=58,235,59
CALL PLOT55(4,1,I)
CONTINUE
500 DO 510 I=1,501,25
CALL PLOT55(5,1-I,1)
CONTINUE
510 DO 15 K=1,512
R(K)=0.
15 CONTINUE
CALL INFR(DATA)
X(1)=FLOAT(DATA(1))-FO
CALL INFR(DATA)
X(2)=FLOAT(DATA(1))-FO
100 CALL INFR(DATA)
X(3)=FLOAT(DATA(1))-FO
IF(X(2)-X(3)) 110,111,111
110 X(1)=X(2)
X(2)=X(3)
GO TO 100
111 EPSLN=3.*(X(1)+X(3))
EPSLN=EPSLN-2.*(X(1)+X(2)+X(3))
EPSLN=(X(3)-X(1))/EPSLN
EPSLN=EPSLN*DDEL
T=TP1*DSIG
TO=T*EPSLN
25 IF(T=TO-TPI) 26,27,27
27 TO=TO-TPI
GO TO 25
26 T=T*DDEL
40 IF(T-TPI) 30,30,35
35 T=T-TPI
GO TO 40
30 N=INT(SIGL/DSIG)
F=FLOAT(N)
THETA=P*T
PT=P*T
S=X(2)
FJT=TO
IF(IRATIO.EQ.0) GO TO 80
CALL ASSIGN(11,'RK0:SAM:DAT')
DEFINE FILE 11 (512,2,UF11)
GO TO 45
80 CALL ASSIGN(10,'RK0:BGS:DAT')
DEFINE FILE 10 (512,2,UF10)
45 CALL TRNSF
IF(IRATIO.EQ.0) GO TO 81
CALL CLOSE(11)
81 CALL CLOSE(10)
FJT=FJT+T
THETA=THETA+PT
S=X(3)
IF(IRATIO.EQ.0) GO TO 85
CALL ASSIGN(11,'RK0:SAM:DAT,O,'OLD')
DEFINE FILE 11 (512,2,UF11)
CALL ASSIGN(10,'RKO:BGS.DAT','0','OLD')
DEFINE FILE 10 (512,2,'U','IF10')
CALL TRNSF
DO 20 K=1,(NPT-2)
CALL INFR(DATA)
S=(FLOAT(DATA(1))-FO)*((FNPT-FLOAT(K))/FNPT
FJT=FJT+T
THETA=THETA+PT
CALL TRNSF
IF(NPLOT.EQ.0) GO TO 20
CALL PLOT55(3,-512,IBUFF)
20 CONTINUE
IF(NPLOT.EQ.0) GO TO 57
PAUSE
IF(NPLOT.EQ.1) GO TO 58
57 CALL PLOT55(3,-512,IBUFF)
PAUSE
58 CALL PLOT55(2,0,2)
CALL PLOT55(2,512,0)
CALL CLOSE(10)
IF(IRATIO.EQ.0) GO TO 70
STOP
END
SUBROUTINE TRNSF
DIMENSION B(512),IBUFF(512),BG(512),BUFF(512)
COMMON B,BG/SUBT/S,THETA,FJT,IBUFF,BUFF,BMAX,IRATIO
P12=8.*ATAN(1.)
200 IF(THETA-P12) 210,210,205
205 THETA=THETA-P12
GO TO 200
210 IF(FJT-P12) 230,230,220
220 FJT=FJT-P12
GO TO 210
230 TJK=THETA-FJT
DO 102 K=1,512
TJK=TJK+FJT
B(K)=B(K)+S*COS(TJK)
IF(B(K)) 105,105,110
105 IBUFF(K)=0
BUFF(K)=0.
IF(IRATIO.EQ.0) GO TO 102
WRITE(11,'K') BUFF(K)
GO TO 102
110 IF(B(K)-BMAX) 120,120,115
115 BMAX=B(K)
120 IBUFF(K)=IFIX(235.*B(K)/BMAX)
BUFF(K)=235.*B(K)/BMAX
IF(IRATIO.NE.0) GO TO 104
WRITE(10,'K') BUFF(K)
GO TO 102
102 CONTINUE
104 RATIO=117.*BUFF(K)/BG(K)
IF(RATIO.GE.32000.) RATIO=235.
IBUFF(K)=IFIX(RATIO)
WRITE(11'K) BUFF(K)
RETURN
END
APPENDIX B
PROGRAM IRFFT
DIMENSION S(1080), IDAT(1080), ADD(512)
EQUIVALENCE (DENOM, AVE), (R, REAL), (FI, FIMAG), (SMIN, REAL),
1 (SUBW, DENOM), (ILOC, N1), (LEN, N3), (JEND, N4), (BR, DR), (BI, DI),
2 (REAL, CR), (FIMAG, CI), (JMAX, JP), (M2, N3), (M1, N4), (M2, JMAX),
3 (FK, FL), (KN, N3), (K1, N4), (K1, N1), (K3, JMAX), (RES, FK), (SMAX, BR)
ICOUNT=0
PI=4.*ATAN(1.)
IBCONT=0
IRCONT=0
IRERUN=0
69 WRITE(7,67)
67 FORMAT(1X,'TO PLOT A RATIOED SPECTRUM ENTER '1',/,'1X,'TO PLOT A
1 BACKGROUND SPECTRUM HIT 'RETURN' KEY')
READ(S,54) IRATIO
54 FORMAT(I1)
IF(IRATIO.NE.0) GO TO 80
WRITE(7,600)
85 WRITE(7,600)
600 FORMAT(1X,'ENTER SIGMAX [PER CM.] AS E15.9')
READ(S,54) SIGMAX
4 FORMAT(E15.9)
IF(SIGMAX-1250.0) 610,615,605
605 WRITE(7,607)
607 FORMAT(1X,'SIGMAX GT 1250 PER CM.--TRY AGAIN')
GO TO 85
610 IF(SIGMAX-625.0) 617,616,615
617 IF(SIGMAX-312.5) 611,620,616
611 IF(SIGMAX-156.25) 612,625,620
612 IF(SIGMAX-78.125) 630,630,625
615 STEP=4.
SIGMAX=1250.
GO TO 635
616 STEP=8.
SIGMAX=625.
GO TO 635
620 STEP=16.
625 SIGMAX=312.5
630 GO TO 635
635 STEP=32.
640 SIGMAX=156.25
645 GO TO 635
649 STEP=64.
650 SIGMAX=78.125
654 WRITE(7,640)
660 FORMAT(1X,'ENTER RESOLUTION DESIRED [PER CM.] AS E15.9')
665 READ(5,4) RES
670 WRITE(7,642)
675 FORMAT(1X,'ENTER SENSITIVITY [IN MILLIVOLTS] AS E15.9')
680 READ(5,4) SEN
685 SEN=SEN/5.
690 IFIX(1./(RES*STEP*1E-04))
695 NPPOW=0
700 NN=NP
705 NNP=NN+1
710 IF(NNP) 655,655,650.
720 NPPOW=NPPOW+1
730 GO TO 645
735 IF(NP,GT.(2**NPPOW)) NPPOW=NPPOW+1
740 NP=2**NPPOW
745 IF(NP,LT.1024) GO TO 659
750 WRITE(7,656)
755 FORMAT(1X,'* OF POINTS TO BE PLOTTED IS GT 512',/1X,'TO RE-START HIT 'RETURN' KEY',/1X,'TO CONTINUE ENTER '1''
770 READ(5,54) IOVER
775 IF(IOVER.EQ.0) GO TO 69
790 IFN=FLOAT(NP)
795 RES=1./(FNP*STEP*1E-04)
800 IF(SIGMAX.EQ.1250.) STEP=8.
WRITE(7,660) STEP,NP,RES,SIGMAX
660 FORMAT(1X,'SET STEP TO = ',F3.0,' MICRONS','/','1X,'NP = ',
1 IS5,' = TOTAL # OF POINTS','/','1X,'ACTUAL RESOLUTION = ',F6.2,
2 ' PER CM.','/','1X,'ACTUAL SIGMAX = ',F8.3,' PER CM.') IF(SIGMAX.EQ.1250.) STEP=4,
NP=NP+IFIX(400./STEP)
START1=1000.*FLOAT(INP)*STEP/200.
START2=1000.*FLOAT(INP)*STEP/200.
IF(IRATIO.NE.0) GO TO 70
ICOUNT=1
ICONT=0
GO TO 71
80 IF(ICOUNT.EQ.0) GO TO 85
WRITE(7,642)
WRITE(5,'(I4) SEN
55 FORMAT(/1X,'SET UP TO RUN RATIO')
SEN=SEN/5.
WRITE(7,55)
70 FORMAT(/1X,'START INTERFEROMETER AT ',F6.1,' TOWARD ZPD AND
71 WRITE(7,670) START1,START2
670 FORMAT(/1X,'START INTERFEROMETER AT ',F6.1,' TOWARD ZPD AND HIT "RETURN" KEY','/1X,'OR','/1X,'START INTERFEROMETER AT ',
1 F6.1,' TOWARD ZPD AND HIT "RETURN" KEY')
PAUSE
WRITE(7,14)
14 FORMAT(1X,'DATA NOW BEING ACQUIRED FROM SPECTROMETER')
VF=2**NPOW
IF(SIGMAX.EQ.1250.) GO TO 30
CALL IRDATA(INP,IDAT)
30 CALL IR4MIC(INP,IDAT)
31 DO 7 I=1,INP
7 CONTINUE
WRITE(7,13)
13 FORMAT(1X,'DATA ACQUIRED FROM SPECTROMETER')
CALL BELL
SMAX=0
DO 9 J=1,INP
  IF(S(J)-SMAX) 9,9,8
  SMAX=S(J)
  JMAX=J
9 CONTINUE
M=NP
N2POW=-1
M=M/2
IF(M) 12,12,11
N2POW=N2POW+1
GO TO 10
10 CONTINUE
N=2**N2POW
N1=JMAX-N
N2=JMAX-3
N3=JMAX+3
N4=JMAX+N-1
FN=FLOAT(N)
AVE=0
DO 22 J=N1,N4
  AVE=AVE+S(J)
22 CONTINUE
AVE=AVE/FN
DO 23 J=N1,N4
  S(J)=S(J)-AVE
23 CONTINUE
DENOM=FLOAT(N2-N1)
DENOM=1./DENOM
DO 40 J=N1,N2
  S(J)=S(J)*DENOM*FLOAT(J-N1)
40 CONTINUE
DENOM=FLOAT(N4-N3)
DENOM=1./DENOM
DO 41 J=N3,N4
  S(J)=S(J)*DENOM*FLOAT(N4-J)
41 CONTINUE
DO 51 J=1,N
  M1=2*J+N1-2
  S(2*J-1)=S(M1)
  M1=M1+1
  S(2*J)=S(M1)
51 CONTINUE
JJ=1
DO 100 I=1,N
  IF(I-JJ) 101,102,102
  R=S(2*JJ-1)
  FI=S(2*JJ)
  S(2*JJ-1)=S(2*I-1)
  S(2*JJ)=S(2*I)
  S(2*I-1)=R
  S(2*I)=FI
101
M=M/2
103 IF(JJ-M) 105,105,104
104 JJ=JJ-M
M=M/2
IF(M-2) 105,103,103
105 JJ=JJ+M
100 CONTINUE
SUBW=2.
ILOC=2
LEND=1
JEND=N/2
200 DO 210 K=1,N2POW
205 ARG=2.*PI/SUBW
210 DO 220 J=1,JEND
200 DO 200 L=1,LEND
FL=FLOAT(L-1)
JP=2*ILOC*(J-1)+2*(L-1)+1
200 JPP=JP+ILOC
WREAL=COS(FL*ARG)
WIMAG=-SIN(FL*ARG)
REAL=S(JPP)*WREAL-S(JPP+1)*WIMAG
FIMAG=S(JPP)*WIMAG+S(JPP+1)*WREAL
S(JPP)=S(JP)-REAL
S(JPP+1)=S(JP+1)-FIMAG
220 CONTINUE
210 CONTINUE
LEND=LEND*2
JEND=JEND/2
ILOC=ILOC*2
SUBW=SUBW*2.
220 CONTINUE
N2=N/2
200 DO 250 M=2,N2
205 M1=2*N+3-2*M
250 M2=2*M-1
200 M11=M1+1
M21=M2+1
250 DR=(S(M21)+S(M11))*0.5
210 DI=(S(M1)-S(M2))*0.5
200 CR=(S(M2)+S(M1))*0.5
250 CI=(S(M21)-S(M11))*0.5
S(M1)=DR
S(M11)=DI
S(M2)=CR
S(M21)=CI
250 CONTINUE
ARG=PI/FN
200 DO 350 K=2,N2
350 FK=FLOAT(K-1)
WREAL=COS(FK*ARG)
WIMAG=-SIN(FK*ARG)
250 KN=2*N+3-2*K
\begin{verbatim}
KI=2*K-1
.REAL=S(KN)*WREAL-S(KN+1)*WIMAG
FIMAG=S(KN)*WIMAG+S(KN+1)*WREAL
BR=S(KI)+REAL
BI=S(KI+1)-FIMAG
HOLD1=SORT(BR*BR+BI*BI)
BR=S(KI)-REAL
BI=S(KI+1)-FIMAG
S(KI)=HOLD1
S(KN)=SORT(BR*BR+BI*BI)
350 CONTINUE
C MIDPOINT MISSED IN TRANSFORMATION [DO 350]. *CORRECTED* BY
C TAKING AVERAGE.
S(2*N2+1)=(S(2*N2-1)+S(2*N2+3))/2.
GO TO 800
730 SMAX=0.
DO 530 I=5,NP,2
IF(((S(I)-SMAX).GE.0.) SMAX=S(I)
530 CONTINUE
SMIN=SMAX
DO 540 I=5,NP,2
IF(((SMIN-S(I)).GE.0.) SMIN=S(I)
540 CONTINUE
DO 500 I=5,NP,2
S(I)=(S(I)-SMIN)/(SMAX-SMIN)*234;
IDAT(I)=IFIX(S(I))
500 CONTINUE
IDAT(1)=0
IDAT(3)=0
GO TO 550
800 S(1)=FLOAT(N)
IF(IRAILO) 300,300,302
300 IF(IBCINT.EQ.0) GO TO 750
CALL ASSIGN(20, 'RK0:BGSFFT.DAT')
DEFINE FILE 20 (S12,2,U,IF20)
DO .720 I=2,N
READ(20'I') ADD(I)
S(2*I-1)=S(2*I-1)+ADD(I)
WRITE(20'I') S(2*I-1)
720 CONTINUE
CALL CLOSE(20)
GO TO 710
750 CALL ASSIGN(20, 'RK0:BGSFFT.DAT')
DEFINE FILE 20 'S12,2,U,IF20)
IF20=1
DO 301 I=1,NP,2
WRITE(20'IF20) S(I)
301 CONTINUE
CALL CLOSE(20)
710 IBCINT=IBCONT+1
GO TO 730
302 IF(IBCINT.EQ.0) GO TO 760
CALL ASSIGN(21, 'RK0:SMFFT.DAT')
DEFINE FILE 21 (S12,2,U,IF21)
\end{verbatim}
DO 765 I=2,N
READ(21'I) ADD(I)
S(2*I-1)=S(2*I-1)+ADD(I)
WRITE(21'I) S(2*I-1)
765 CONTINUE
CALL CLOSE(21)
GO TO 770
760 CALL ASSIGN(21,'RK0:SA.MFF,T.DAT')
DEFINE FILE 21 (S12,2,U,IF21)
IF21=1
DO 303 I=1,NP,2
WRITE(21'IF21) S(I)
303 CONTINUE
CALL CLOSE(21)
770 IRCONT=IRCONT+1
GO TO 730
550 CALL PLOT55(2,0,2)
CALL PLOT55(2,512,0)
CALL PLOT55(1,0,0)
CALL PLOT55(2,1+2+32+64,0)
CALL PLOT55(7,0,0)
CALL PLOT55(9,0,0)
CALL PLOT55(10,0)
CALL PLOT55(9,0,23)
CALL PLOT55(4,1,0)
DO 501 I=58,235,59
CALL PLOT55(4,1,I)
501 CONTINUE
DO 510 I=1,501,25
CALL PLOT55(5,I-1,1)
510 CONTINUE
DO 520 I=3,512,(512/N)
IF(I.GT.3) GO TO 515
J=1
515 CALL PLOT55(3,I-3,IDAT(J))
J=J+2
520 CONTINUE
PAUSE
CALL PLOT55(2,0,2)
CALL PLOT55(2,512,0)
IF(IRATIO.EQ.0) GO TO 795
CALL SRATIO
CALL SRATIO
WRITE(7,780) IBCONT
780 FORMAT(1X,'REFERENCE SPECTRA RUN ',I3,' TIMES')
WRITE(7,785) IBCONT
785 FORMAT(1X,'SAMPLE SPECTRA RUN ',I3,' TIMES',//)
WRITE(7,790)
700 FORMAT(1X,'TO RE-RUN TO OBTAIN AVERAGED SPECTRA HIT 'RETURN' KEY
1 '/,1X,'TO CONTINUE ENTER '1''
READ(5,54) IRERUN
IF(IRERUN.EQ.0) GO TO 71
IF(IRATIO.EQ.0) GO TO 69
WRITE(7,304)
704 FORMAT(1X,'TO PLOT RATIO RUN PROGRAM 'RATIO'')
WRITE(7,810)
810 FORMAT(1X,'TO PLOT REFERENCE SPECTRUM RUN PROGRAM 'PBFFT'')
WRITE(7,820)
820 FORMAT(1X,'TO PLOT SAMPLE SPECTRUM RUN PROGRAM 'PSFFT'')
STOG
END
.MCALL ..V2..,.REGDEF,.PRINT,.EXIT
..V2..
.REGDEF
.GLOBL IRDATA
ADSR=170400
ADDR=170402
IRDATA: CLR R4
        ADD $2, R5
        MOV @(R5)+, R1
        MOV (R5), R2
        MOV $20, @ADDR
LOOP:   TSTB @ADDR
        BPL LOOP
        MOV @ADDR, (R2)+
        BIT $100000, @ADDR
        BNE ERROR
        INC R4
        CMP R4, R1
        BNE LOOP
        MOV (R5), R2
AGAIN:  SUB $4000, (R2)+
        DEC R4
        CMP R4, $0
        BNE AGAIN
        RTS PC
ERROR:  .PRINT #FAIL
FAIL:   .ASCIZ /FLAG OVERRUN BIT SET - SOME DATA LOST/
        .EVEN
        .EXIT
        .END
.MCALL ..V2...REGDEF,.PRINT,.EXIT
..V2..
.REGDEF
.GLOBL IR4MIC

ADSR=170400
ADBR=170402
CLKSR=170420
CLKBUF=170422
IR4MIC: CLR R4
CLR R0
CLR @@CLKBUF
ADD #2,R5
MOV @(R5)+,R3
MOV (R5),R2
MOV #20036,@@CLKSR

CLK: TST @@CLKSR
BPL CLK
BIC #100000,@@CLKSR

NEXT: MOV #20,@@ADSR

LOOP: TSTB @@ADSR
BPL LOOP
MOV @@ADBR,(R2)+
BIT #100000,@@ADSR
BNE ERROR
INC R4
CMP R4,R3
BEQ DONE
ADD @@CLKBUF,R0
MOV R0,R1
CLR RO
DIV @2,R0
NEG RO
CLR @@CLKSR
MOV RO,@@CLKBUF
NEG RO
MOV $40,@@ADSR
MOV $31,@@CLKSR
HALF:
   TSTB @@ADSR
   BPL HALF
   MOV @@ADBR,(R2)+
   BIT $100000,@@ADSR
   BNE ERROR
   INC R4
   CMP R4,R3
   BEQ DONE
   MOV $37,@@CLKSR
   JMP NEXT
DONE:
   MOV (R5),R2
AGAIN:
   SUB $4000,(R2)+
   DEC R4
   CMP R4,$0
   BNE AGAIN
   RTS PC
ERROR:
   .PRINT @FAIL
FAIL:
   .ASCIZ /FLAG OVERRUN BIT SET - SOME DATA LOST/
   .EVEN
   .EXIT
   .END
Chapter I


2. Ibid., p. 3.


8. (Lattice Constants of CaF$_2$, SrF$_2$, and BaF$_2$).


30. G. Raca, Phys. Rev. 61, 186 (1942); ibid. 62, 438 (1942);
    ibid. 63, 367 (1943); ibid. 76, 1352 (1949).
34. Reference 7, p. 48.

Chapter II

Chapter III
Chapter IV


Chapter VI


**Vita Auctoris**

<table>
<thead>
<tr>
<th>Date</th>
<th>Event Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>October 24, 1940</td>
<td>Born in Hamtramck, Michigan, USA.</td>
</tr>
<tr>
<td>1961-1966</td>
<td>Military Service</td>
</tr>
<tr>
<td>1966-1970</td>
<td>Employed by IBM Corporation</td>
</tr>
<tr>
<td>1972</td>
<td>Graduated from the University of Detroit with a B.Sc. Degree.</td>
</tr>
<tr>
<td>1974</td>
<td>Graduated from the University of Detroit with an M.Sc. Degree.</td>
</tr>
<tr>
<td>1974</td>
<td>Began Ph.D. studies, University of Windsor, Ontario, Canada.</td>
</tr>
<tr>
<td>1980–</td>
<td>Employed by University of Detroit.</td>
</tr>
</tbody>
</table>