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THE INFRARED SPECTRUM OF SOLID HYDROGEN DEUTERIDE

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By
Koon Kai Lo, B.S., M.S.

* * * * *

The Ohio State University

1983

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CHAPTER I

INTRODUCTION

The solid hydrogens which are comprised of molecular hydrogen, hydrogen deuteride and molecular deuterium are the simplest molecular solids and present unique opportunities for the study of lattice dynamics and intermolecular interactions in the crystalline state. A characteristic property of the hydrogen solids is that the rotational motion of the molecules is free in the sense that the quantum number $J = \sum J_i$, where $J_i$ is the rotational quantum number of molecule $i$ and the sum extends over all the molecules, is a good quantum number. This free rotation persists down to the absolute zero of temperature, and is quite different from the free rotation observed in many molecular crystals at sufficiently high temperatures. In the hydrogen solid the effect of anisotropic intermolecular interaction is small compared to the separation of the rotational levels that states corresponding to different values of $J$ are not mixed appreciably. Similar remarks apply to the internal vibrational motion of the molecules characterized by the vibrational quantum number $v$. This
remarkable state is a consequence of the large molecular rotational constant, which is due to its small moment of inertia, and the small anisotropic intermolecular forces which are a result of the almost spherical charge distribution and the relatively large intermolecular nearest neighbor distance, about 3.66 Å in the zero pressure HD solid (1).

The necessary condition for a molecule to have an ordinary infrared absorption is that the molecule possesses a dipole moment. Homonuclear diatomic molecules such as hydrogen and deuterium do not exhibit ordinary electric dipole infrared spectra corresponding to molecular rotation or vibration in the free state because of the symmetry of their charge configuration in their ground electronic states. However, these molecules when compressed in their pure state or in their normal pressures liquid or solid phases give rise to infrared spectra due to electric dipoles induced in two or more molecules by intermolecular forces mainly because of (i) the overlap of the electron clouds, and (ii) the quadrupolar induction resulting from the polarization of one molecule by the multipole field of the other.

Although the HD molecule, just as the H₂ and D₂ molecules, has no electric dipole moment in the equilibrium position in its ground electronic state, a weak, oscillating
dipole moment results in it because, during a molecular vibration, the displacements of the proton are greater than those of the deuteron and the negative charge center of the electrons lags behind the positive charge center of the nuclei. The HD molecule is heteronuclear and hence for it the distinction between symmetric and antisymmetric rotational levels which is important in H\textsubscript{2} and D\textsubscript{2} does not exist. That is, there are no para or ortho modification of HD. The occurrence of a rotation-vibration spectrum of HD due to its oscillating electric dipole moment was first predicted by Wick (2). Weak rotation-vibration absorption bands of HD were first observed by Herzberg (3) near 9650 and 7400 Å and were identified as the 3-0 and 4-0 bands, respectively. Later, the pure rotational spectrum of HD was observed by Trefler and Gush (4) who determined the dipole moment of HD by measuring the integrated intensities of four R\textsubscript{0} lines. Subsequently, McKellar (5) made a comprehensive study of the 1-0, 2-0, 3-0 and 4-0 bands of HD and measured the intensities of 13 electric dipole transitions and one quadrupole transition. Bejar and Gush (6) also measured independently the intensities of 5 electric dipole transitions of the 1-0 band of HD. Recently, Nelson and Tabisz (7) reported new measurements on the pure rotational spectrum of HD and demonstrated the J dependence of the dipole moment of the molecule in its ground vibrational state. The selection rule for the rotational transitions arising from the electric dipole moment is \( \Delta J = \pm 1 \) and that
for the transitions arising from the electric quadrupole moment is \( \Delta J = 0, \pm 2 \), where \( \Delta J \) represents the change in the rotational angular momentum between the upper and the lower states.

According to the theory of the collision-induced absorption of diatomic gases proposed by Van Kranendonk (8), the dipole moment induced in a colliding pair of molecules is represented by the so called "exponential-4" model. In this model, the induced dipole moment consists of two additive parts. One part is the isotropic short-range overlap moment which decreases exponentially with increasing intermolecular separation \( R \) and the other part is the anisotropic long-range moment, resulting from the polarization of one molecule by the quadrupole field of the other molecule, which varies as \( R^{-4} \). The short-range moment contributes mainly to the intensity of the broad \( Q \) (i.e. \( Q_{\text{overlap}} \) \( (\Delta J = 0) \)) lines. The long-range moment contributes to the intensity of the relatively less broad \( 0 \) (\( \Delta J = -2 \)), \( Q \) (i.e. \( Q_{\text{quad}} \) \( (\Delta J = 0) \)), and \( S \) (\( \Delta J = +2 \)) lines. Based on this model, Van Kranendonk (9) calculated the integrated intensities of the infrared rotational and vibrational spectra of the \( Q \) and \( S \) bands of solid parahydrogen.

The solid hydrogens form a class of solids known as quantum crystals. These solids are characterized by the property that the amplitude of the zero-point lattice vibration is an appreciable fraction of the lattice constant...
as a result of the small mass of the molecules and the relatively weak intermolecular forces. Shortly after the first observed hexadecapolar induced $U_{v'-v''}(0)$ ($v'-v''=0,1$ and $J'-J''=4$) transition in solid parahydrogen by Reddy et al. (10), Poll and Tipping (11) using Van Kranendonk's theory, calculated the integrated intensity of the $U_{v'-v''}(0)$ line and its phonon branch by incorporating a "reduction factor" $\xi=0.8$ for nearest neighbors and $\xi=1$ for other molecules. This expression leads to an intensity that is smaller than the more accurate high resolution measurements of Ivancic et al.(12) by almost a factor of 0.6.

Balasubramanian et al. (13) using Gray's (14) derived formula for the induced moment between two nonoverlapping charges calculated the integrated intensities for the $U_{v'-v''}(0)$ ($v'-v''=0,1$) and $U_{0}(1)$ transitions in para-$H_2$ and normal-$H_2$ which are in good agreement with the experimental values. This method has further advantage over the former in that the infrared activity of individual sublevels is automatically included in the derivation.

The induced dipole moments depend not only on the orientation of pairs of neighboring molecules but also strongly on the intermolecular separation. This distance dependence gives information about the collective motions of molecules in the solid hydrogens lattice. In a given spectral region, the infrared absorption of solid hydrogens will typically consist of two parts: one may be a sharp
line while the other is a broad band lying to the high frequency side of the sharp line. The sharp line is interpreted to be a single or double rotational vibration transitions without any phonon involved in the process and it is termed the "zero phonon transition". The accompanying broad band is interpreted as a transition involving a molecular excitation accompanied by the creation of one or more phonons in the crystal. Historically this band has been called the "phonon branch". A theory of the phonon branches of solid parahydrogen has been developed by Poll and Van Kranendonk (15) who derived general expressions for the integrated intensities and calculated the integrated absorption coefficient on the basis of the Einstein and isotropic Debye models for the lattice vibrations. The lattice vibrations in the solid hydrogens affect the rotational and internal vibrational motions of the molecules in a number of ways. In particular, a resonance interaction occurs when the rotational excitation energy falls below the maximum phonon frequency, as is true for the J=1 rotons in HD. A more detailed account on this subject will be given in the following chapters.

The phonon branches of the induced infrared spectrum can be regarded as combination tones of the fundamental rotation-vibration frequency of the molecule with the phonon frequency. The intensity of the branch which arises due to the creation of a single phonon thus depends on the matrix
element of the induced dipole moment and the number of energy states available to the phonon in the final state. Since the density of these states is essentially determined by the lattice vibrational spectrum it is possible to express the intensity of the phonon branch in terms of the lattice vibrational spectrum. The calculation of this intensity is presented in Chapter III.

The magnitude and orientation of the induced dipole moment depends on the coordinates of the molecules in the lattice. It is then possible to have transitions in which two or more molecules simultaneously change their internal energy; these are called double transitions and are quite important in the spectrum of solid hydrogens where they contribute to a large fraction of the intensity of the fundamental band. In a double transition, one molecule makes a vibrational transition and a neighboring molecule makes a rotational transition. The rotational excitation is not localized on any one particular molecule but travels through the lattice by passing from one molecule to another. As a result the upper state of this double transition is a broad exciton band. The frequency of the single transition is lower than the double transition because of the rotation-vibration interaction which lowers the frequency of a vibrating molecule. The single transitions are weak in comparison with the double transitions. This is because of a partial cancellation of the matrix elements of the induced
dipole moment for a single transition. The molecule making the transition is surrounded by a symmetrical arrangement of molecules; the dipoles which it induces in its neighbors tend to cancel because they point in different directions. If the lattice possessed a center of inversion symmetry the cancellation would be complete and single transition such as $Q_{1-0}(0)$ in solid hydrogens would be absent. However, due to quadrupolar induction through the anisotropic interaction, some absorption may be possible as is observed experimentally.

Since the first experimental study of HD in the solid phase by Crane and Gush (16) who reported the infrared absorption spectra of deuterium and hydrogen deuteride in the fundamental band using a grating spectrometer with a resolution of 0.3 cm$^{-1}$, the work on solid HD had been very limited. In this thesis we report the first observation of the $T(\Delta J=3)$, $U(\Delta J=4)$ and $V(\Delta J=5)$ induced infrared transitions in solid HD using a Fourier transform spectrometer operating at a resolution of 0.04 cm$^{-1}$. It is the absorption features arising from the anisotropic intermolecular interaction in solid HD with which this thesis is concerned.

The thesis is organized into five chapters, including the Introduction. In Chapter II, the experimental apparatus and techniques are described together with the procedures for making the HD sample. The measurements reported here
are the first ones made on solid HD using a Fourier transform spectrometer over the entire region 500-5000 cm\(^{-1}\).

In Chapter III, a theoretical basis for the interpretation of the experiments is laid. In that chapter, we will use the derived formula by Gray (14) to calculate the integrated intensities of the T, U and V transitions then use Van Kranendonk's model to calculate that of the R transitions in solid HD.

In Chapter IV, graphs of the experimental data are presented along with a detailed analysis of the spectra.

Finally, in Chapter V, a general discussion of the experimental results and the interpretation of the results based on the theoretical treatment are presented.
CHAPTER II

EXPERIMENTAL METHODS AND APPARATUS

The experiments reported in this thesis were carried out with a liquid helium cryostat, a high sensitivity Fourier transform spectrometer, an absorption cell and some necessary apparatus for sample preparation. In this chapter a description of the apparatus and experimental method will be presented.

II.1 The sample cell

The sample cell used in these experiments was made from a brass cylinder 1.5 inches in diameter and 1.2 inches in length. The brass cylinder was milled to give a rectangular cavity with a sample path length of 26 mm. and a cross sectional area of 3/4 in. \times 3/8 in.. The details of the construction of this cell are shown in Fig. 1. The sample cell was supported by the gas fill tube made of a stainless steel capillary tube, 1/16 inch in diameter, which was silver-soldered to the center top portion of the sample cell body. On the center bottom portion of the sample cell,
Figure 1. The sample cell

- **c** Brass sample cell
- **g** Gas fill tube
- **s** Allen head screws
- **r** Brass ring
- **h** Heater coil
- **b** Copper box
- **d** Temperature sensor diode
- **L** Liquid helium capillary tube

SIDE VIEW

FRONT VIEW
there was a needle point of a tapered copper rod which was thermally connected to the ancillary liquid helium chamber. This needle point served as the coolest spot of the sample cell in order to help to form a seed crystal. From this seed crystal, the whole optically clear crystal was grown. With the relatively low thermal conductivity of brass compared to copper, a temperature gradient necessary to grow a clear crystal was established vertically.

A 100 ohm heater coil wrapped around the outside of the cell and up the gas inlet and a helium flow control valve which controlled the amount of liquid flowing through copper box gave the required temperature control. Two calibrated diodes attached to the top of the sample cell and the copper box below were used to measure the temperature of the sample cell. Experiments reported here were under zero external pressure and $T = 16^\circ K$ for HD.

Two optically flat silver chloride plates 1 inch in diameter and 1/4 inch thick constituted the entrance and exit windows. The silver chloride windows were attached to the polished window seat of the cell which had a circular aperture of $1\frac{1}{16}$ inches in diameter. An indium ring provided the necessary sealing between the window and the seat. In order to obtain a pressure-tight seal between the window seat and the silver chloride window, a brass ring was placed on top of the window and was tightened against the cell
body by means of 12 Allen head screws.

In the present experiment, finding suitable windows for the sample cell had been a vexing problem. This was because they had to withstand the thermal strain of cooling to liquid helium temperature and the mechanical stress when they were pressed against indium gasket to provide a vacuum seal as well as to transmit in the infrared. Sapphire windows used earlier would not transmit in the pure rotational transition region. However, windows made of silver chloride were found to serve this purpose.

II.2 The Liquid Helium Cryostat

A schematic diagram of the liquid helium dewar made by the Janis Research company and the sample cell in its tailsection is shown in Fig.2. The main body of the dewar consists of six concentric chambers. The innermost chamber through which electrical wires, the sample fill tube, and the helium gas escape tube pass, is surrounded by a vacuum chamber, a liquid helium reservoir, a second vacuum chamber, a liquid nitrogen reservoir, and a third (outermost) vacuum chamber. A special tail section is attached to the main body of the cryostat. It contains the brass sample cell supported by the sample gas stainless steel fill tube. A length of sample cell up to 10 cm. can be accommodated in this tailsection comfortably. The tailsection also has two
Figure 2. Liquid Helium Cryostat
(See next page for description)
optically flat windows that transmit the radiation and also act as vacuum seals. These windows must be selected from a material which transmits the appropriate band of infrared radiation. Since our primary interest is in the 5-50 μm region, we chose our window materials to be silver choride, strontium fluoride and KRS-5.

Temperature between 1°K and 20°K can be obtained conveniently with this cryostat. This is potentially an advantage over the previous infrared absorption experiments of solid hydrogen but it was not exploited here.

II.3 Hydrogen Deuteride Preparation

Hydrogen deuteride was prepared by the action of D₂O on LiAlH₄ as described by Fookson et al. (16). The chemical reaction governing the formation of HD gas was the following:

\[
\text{LiAlH}_4 + 4\text{D}_2\text{O} \rightarrow \text{LiOD} + \text{Al(OD)}_3 + 4\text{HD}
\]

The amounts of lithium aluminum hydride and deuterium oxide used depended on the amount of hydrogen deuteride required. Normally, for 15 liters of HD, half a mole (6 grams) of lithium aluminum hydride and 2 moles (20 grams or 70 c.c.) of deuterium oxide would suffice. However, it was desirable to use a somewhat excess amount of LiAlH₄ in order to prevent the reaction from becoming too sluggish as the
reagents were consumed. Besides these two major ingredients, a third chemical, butyl ether \((\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{O}\) was essential. Butyl ether served only as a catalyst. It would not take part in the chemical reaction.

The apparatus used in the preparation of hydrogen deuteride is shown in Fig. 3. Before each run, several things had to be done. First, the system was checked for vacuum leaks. If leaks developed or small cracks appeared in the glassware, these had to be repaired using standard glass blowing techniques. Glass stopcocks were cleaned with ether and regreased when turning became difficult. A cold gas flame was used to bake the remaining glassware and the system was subsequently purged two or three times with argon gas to ensure that the system was free from impurities. The entire system was then evacuated (stopcocks A, C, D, E, F open and B, G, H closed). Stopcocks C, D and E, F for the two collecting bulbs were closed as the system was pumped down to the desired pressure, usually in the 2-4 torr range. After this was accomplished, stopcock B was opened and the whole system except the two collecting bulbs was opened to the atmosphere. About 150 c.c. of butyl ether was introduced into the flask I through the septum-retaining device J by means of a plastic funnel to avoid possible contact of the chemicals with the stopcock grease. This was then followed by 6 grams of lithium aluminum hydride. About 80 c.c. of deuterium oxide was poured into container L through the
Figure 3. Preparation of Hydrogen Deuteride
septum-retaining device K (stopcock G closed).

A basin containing water and ice cubes was placed under the flask I to ensure the reaction temperature was kept at 0°C or lower. This would decelerate the chemical reaction. After these were accomplished, cold traps (M and N) were immersed in dewars containing liquid nitrogen and the entire system was pumped down to the desired pressure (a few Torr). During this time, all of the stopcocks except stopcock A are closed. The system was then filled with argon gas (stopcock A closed and B open). This last operation was continued until the pressure in the system as read on the pressure gauge was about 2/3 of an atmospheric pressure (stopcock B then closed). By opening and closing the stopcock G, a few drops of D$_2$O were added to the reaction mixture, and gas evolved as a consequence of the reaction. The pressure inside the system should be kept at less than one atmosphere during the whole course of the reaction to prevent blowing out of the stopcock or explosion due to high gas pressure. To do this, the stopcock A loading to the vacuum pump was opened slowly and then closed allowing part of the gas to be pumped out. Since the partial pressure of the argon gas was proportional to the volume, the argon gas molecules inside the system were reduced proportionally. This process of opening and closing was repeated ten times or more until all traces of argon were removed from the system. During the course of the reaction, deuterium oxide
was added several times, to make a total of 40 c.c. of this reagent added and during the whole operation, the mixture was being stirred continuously. Due to its low temperature, the outside of the flask quickly accumulated a layer of frost. Whenever this began to melt, ice cubes were added; in this manner, the reaction temperature was kept at 0°C or lower. The HD gas evolved from the reaction was then collected in two 5-liter collecting bulbs by opening and closing the stopcock pairs E, F and C, D in succession. It was assumed that a 6 to 8% of H₂ and D₂ impurities were present in the two batches prepared. This became evident when spectral features were found which correspond to combinations of HD-H₂ and HD-D₂ frequencies. Other impurities such as air, were removed by distillation.

During the experiment, the sample cell was placed in the optical path of a Fourier transform spectrometer. Sample gas which was stored in a 5 liter glass flask was condensed and solidified by boiling of liquid helium flowing through a copper box under the sample cell. A tapered copper rod thermally connected to the sample cell and the copper box below gave the required temperature control. The cooling rate was maintained at an extremely slow rate, when the sample was about to solidify. In this manner, it was possible to make a good optical-quality crystal. It took about 1 to 2 hours from the starting of solidification to
completely solidify the sample. After the crystal was grown, the temperature was maintained around the freezing point (16°K for HD) to make sure we had a clear crystal through the entire data taking period.

The frequency calibration was obtained by using the $\nu_2$ band lines of the carbon dioxide in the region 600 to 700 cm$^{-1}$.

II.4 The Fourier Transform Spectrometer

In this section, an outline will be given of the principle of operation of a Fourier transform spectrometer (FTS). For a more detailed account, the reader is referred to the standard textbook by Bell (18). Also all of the material in this section is available in the manual for the Nicolet 7000 FTS (19) and the technical report on "Fourier Transform Spectroscopy" by Chaney (20).

There are two major advantages that the interferometer has over the conventional dispersive grating spectrometer. These are:

(1) The multiplex or Fellgett advantage

The basis of the advantage is that in observing a spectral element the increase in signal to noise ratio, S/N, is proportional to the square root of the elemental observation time $t$. If the different spectral elements are
explored consecutively, as is done in a conventional spectrometer, the time available for each spectral element is $t/M$, where $M$ is the number of spectral elements. The interferometer, however, observes all the spectral elements simultaneously for the total time $t$. Since the signal to noise is proportional to the square root of the observation time, then the gain $G=(M)^{1/2}$, where $M$ the number of resolution elements is exactly equal to the increase in observation time.

This advantage assumes that the noise is independent of the signal falling on the detector. The assumption is true for thermal detectors such as thermocouples and thermistor bolometers but not true for photon detectors. For this reason, the interferometer has found its greatest application in the infrared. The gain can be substantial if a wide spectral region is to be scanned. Therefore, the greatest advantage of the FTS is its ability to measure many features, spread over wide spectral regions, simultaneously.

(2) The throughput or Jacquinot advantage

The throughput of an optical instrument is a measure of the amount of light transmitted by an instrument having a given aperture and a given solid angle. The throughput can be expressed by

$$TP = \frac{\Phi}{B} \quad (2.1)$$
where $\phi$ is the flux falling on the detector and $B$ is the intensity of the source. In terms of the optical instrument

$$TP = A\Omega T$$

(2.2)

where $A$ is the area of the aperture, $\Omega$ is the solid angle, and $T$ is the transmission factor and Eq.(2.1) is equal to Eq.(2.2). The transmission factor is actually the product of a number of factors and would be one for a perfect instrument.

It is apparent that any increase in the solid angle will increase the throughput. However, for a spectrometer the permissible solid angle is limited since an increase in solid angle will decrease the spectral resolution. Thus, the product of the resolution $R$ and the solid angle $\Omega$ is a constant. The advantage that the interferometer achieves is due to the fact that the product $R\Omega$ is much larger (two orders of magnitude) than in a grating spectrometer.

Interferometer \hspace{1cm} R\Omega = 2\pi

Grating Spectrometer \hspace{1cm} R\Omega = 0.07

In this way, more radiation can go through the interferometer to the detector and for a weak absorption give a better S/N ratio.

The interferometer we used is a Nicolet 7000 FTS. It
uses a two beam scanning Michelson interferometer. An optical layout of Nicolet interferometer is shown in Fig.4. It contains three scanning Michelson interferometers—a main infrared interferometer, a He-Ne laser interferometer, and a white light interferometer. The two visible interferometers (optical elements: M₃, M₄, M₅, M₆, BS_W and BS_L) are used to control the sampling logic and the scanning of the moving mirror.

The main infrared interferometer consists of two perpendicular plane mirrors M₁ and M₂ and a beamsplitter BS_M mounted at 45 degrees to mirrors M₁ and M₂. M₁ is stationary while mirror M₂ is scanned at constant velocity V. The basic operation is as follows: The input radiation represented by the ray B is brought to the interferometer on an optical axis perpendicular to mirror M₂. The beamsplitter divides the incident beam into two separate beams, one passing to mirror M₁ and the other to mirror M₂. Each ray is returned to the beamsplitter and divided again. Two recombined beams are thus formed. One recombined beam is reflected back towards the input and lost while the other beam passed through the sample cell and to the detector. The moving mirror is normally displaced through a distance ± L/2 from a point of zero retardation such that the optical path difference is equal to ± L; therefore when the two beams are recombined they interfere. The intensity I(δ, λ) of the exit beam with path difference δ and incident wavelength λ can be
Figure 4. Optical set up of the FMS 7001P interferometer
expressed as follows:

\[ I(\delta, \lambda) = 0.5 \ H(\lambda) \ B(\lambda) \left[ 1 + M(\lambda) \ \cos\left( \frac{2\pi \delta}{\lambda} + \theta_\lambda \right) \right] \]

where \( B(\lambda) \) is the intensity of the incident beam, \( H(\lambda) \) (less than unity) represents the departure from the actual intensity \( B(\lambda) \) due to instrument characteristics, \( \theta_\lambda \) is a phase shift instrument function (unavoidable phase shifts from beamsplitter, detector and electronics), and \( M(\lambda) \) (less than unity) is the modulation efficiency that represents the departure from theoretical performance of the beamsplitter and optical system.

In a scanning Michelson interferometer, \( \delta \) is varied continuously by moving mirror \( M_2 \) at a constant speed. The effect of this sweeping is to modulate the output intensity \( I(\delta, \lambda) \) in a sinusoidal fashion with a frequency \( f(\lambda, v) \) that depends on wavelength \( \lambda \) and mirror velocity \( v \),

\[ f(\lambda, v) = \frac{2v}{\lambda} \]

Normally, the incident beam is not a single frequency but a broad band source with a continuum of energy with respect to wavelength. Yet each frequency is modulated independently and can be sorted from the continuum by a Fourier transform. Because of this independence, the modulated exit beam may be focused directly on an infrared detector without monochromatic filtering for a specific wavelength. The entire incident spectral information is
recorded in a multiplexed form by the detector during a scan of the moving mirror. The detector output as a function of optical path displacement is called an interferogram, \( \text{IGM}(\delta) \). A typical interferogram from our experiments is shown in Fig. 5. The amplitude \( \text{IGM}(\delta) \) of the interferogram recorded at some point \( \delta \) and its amplitude \( I(\nu) \) recorded at a wave number \( \nu \) are related by the Fourier transform and are written mathematically as a cosine Fourier transform pair as follows:

\[
\text{IGM}(\delta) = \int_{-\infty}^{\infty} I(\nu) \cos 2\pi \nu \delta d\nu
\]

and

\[
I(\nu) = \int_{-\infty}^{\infty} \text{IGM}(\delta) \cos 2\pi \nu \delta d\delta
\]

These are the basic equations upon which Fourier transform spectroscopy is based. The equations, however, imply that the length of the mirror drive is infinite, which is impossible. In the case of a real interferometer, the interferogram is recorded for a finite length \( L \) of mirror travel. The effect of this limitation is to limit our spectral resolution to \( L^{-1} \). If the maximum distance from a position of zero retardation is \( L \), Eq. (2.3) becomes

\[
I'(\nu) = \int_{-\infty}^{\infty} \text{IGM}(\delta) \cos 2\pi \nu \delta d\delta
\]

In general, \( I'(\nu) \) will be different from the observed spectra \( I(\nu) \). \( I'(\nu) \), however, can be written as the convolution of \( I(\nu) \) and a scanning function \( t(\nu) \) in the following way,
Figure 5. Interferogram of 93% HD and 7% $H_2$ sample
\[ I'(\nu) = t(\nu) * I(\nu) \]

The most commonly used truncation function is a triangular function which produces a \( \left( \frac{\sin x}{x} \right)^2 \) scanning function (Fig. 6). With the introduction of the truncation function, the new equation which expresses the convolved spectra becomes

\[ I'(\nu) = \int_{-\infty}^{\infty} T(\delta) IGM(\delta) \cos 2\pi \nu \delta d\delta \]

The interferogram is then sampled at equally spaced intervals with an analog to digital converter system. These intervals must be spaced close enough so that the complete interferogram is accurately represented by the sampled points. This sample spacing is controlled by a He-Ne laser fringe reference system which assures correct sample accuracy as well as wavelength accuracy in the resultant spectra. The fact that the incident beams have a finite bandwidth allows us to use the sampling theorem to specify a minimum necessary sampling spacing. The Nyquist criterion is

\[ v_{sp} \geq 2 v_{bw} \]

where \( v_{bw} \) is the bandwidth of the IR incident beam and the sampling frequency. Or in terms of optical path difference the sample spacing \( \delta_{sp} \) must satisfy
Figure 6. Triangular truncation function (a) and its Fourier transform (b)
Once the interferogram is digitized and stored, a complex Fourier transform using a Fast Fourier Transform algorithm can be performed on the interferogram by the computing system to decode the multiplexed information to obtain a complex spectrum

\[ \frac{1}{\delta_{sp}} \geq 2 \nu_{bw} \]

\[ I'(u) + jI_i'(u) = \int_0^\infty T(\delta) IGM(\delta) e^{-2\pi j \delta} d\delta \tag{2.4} \]

Normally, the lack of synchronization between the digitizing command and the interferogram as well as the electrical phase shifts in the amplifiers will introduce asymmetry in the interferogram. The Fourier transform of \( I'(u) \) assumes the following expression

\[ IGM(\delta) = \int_0^\infty I'(u) \cos(2\pi \delta u + \Theta_v) du \tag{2.5} \]

where \( \Theta_v \) is the phase shift due to instrumental effects. Combining equations (2.4) and (2.5) we obtain the following identities,

\[ I_R'(u) = I'(u) \cos \Theta_v \]

\[ I_i'(u) = I'(u) \sin \Theta_v \]

To eliminate the instrumental effects that introduced the phase angle \( \Theta_v \) one has to perform the process of phase correction. In this process \( \Theta_v \) is measured as a property of the instrument and then one can calculate \( I'(u) \) by
\[ I'(u) = I_R'(u) \cos \Theta_v + I_I'(u) \sin \Theta_v \]

In this way \( I'(u) \) can be calculated from the measured interferogram \( \text{IGM}(\delta) \).
CHAPTER III

THEORY

The present chapter is devoted to give an overview of the theories for the interpretation of the experimental results. Since the infrared absorption features in solid HD are due to anisotropic intermolecular forces we begin in Section 1 with a discussion of the anisotropic forces between HD molecules. It is found that the angle-dependent terms in the pair potential arising from the mass asymmetry of an HD molecule is responsible for $\Delta J=1$ transitions in solid HD. In Section 2, we discuss the rotational waves in the $J=0$ lattice of solid HD assuming the centers of mass of the HD molecules are held fixed at the sites of a rigid hexagonal close-packed (h.c.p.) lattice.

As mentioned earlier, the infrared absorption spectrum of solid HD is active by virtue of the electric dipole moments induced by intermolecular forces. The experimentally measured amount of absorption is the integrated absorption coefficient $\bar{\alpha}$, defined by the relation

$$\bar{\alpha} = \frac{(c/N_1)}{\int (1/\nu) \ln(I_0/I) \, d\nu}$$
where \( c \) is the speed of light, \( N \) is the number of molecules per \( \text{cm}^3 \), \( l \) is the length of the sample, \( \nu \) is the wavenumber and \( I \) and \( I_0 \) are the transmitted and incident intensities.

In order to develop a theoretical expression for \( \tilde{a} \), we derive in Section 3 an expression for the induced dipole moment. In Section 4 theoretical expressions for integrated absorption coefficient of various zero-phonon transitions are derived assuming that the induced dipole moments are additive. In Section 5 we give a theoretical expression for integrated intensity of the \( \Delta J=1 \) transition based on the Van Kranendonk's model. The phonon branch accompanying the zero-phonon transition is also of interest from the point of view of the general theory of lattice vibration. In particular, a resonance interaction occurs when the rotational excitation energy falls below the maximum phonon frequency. In Section 6 this aspect is discussed following the theory developed by Zaidi (21). Finally, the chapter is concluded in Section 7 with the calculation of the intensity of one-phonon branch in terms of the lattice vibrational mode.

III.1 Anisotropic Forces in Solid Hydrogen

Deuteride

The anisotropic forces between a pair of HD molecules in the \( J=0 \) rotational state result from the displacement,
\( \Delta = 0.123 \, \text{\AA} \), of the charge center from the mass center in the heteronuclear HD molecule. Therefore, the intermolecular potential, \( V(R) \), where \( R \) is the distance between the charge centers of the molecules is not isotropic with respect to \( \vec{R}_o \), the vector joining the two centers of mass.

Consider first the interaction potential for HD in terms of centers of charge coordinates. Assuming the molecules to be permanently in their ground electronic states and in their ground vibrational states, the potential energy of the system can be considered to be a given function of the nuclear configuration,

\[
V = V(\vec{\Omega}_1, \ldots, \vec{\Omega}_N, \vec{r}_1, \ldots, \vec{r}_N) = V(\vec{\Omega}_N, \vec{r}_N) \tag{3.1}
\]

where \( \vec{\Omega}_i = (\theta_i, \phi_i) \) denotes the orientation of the \( i \)-th molecule relative to axes fixed in space, \( \vec{r}_i \) denotes the position of the center of charge of the \( i \)-th molecule, and \( N \) is the total number of molecules in the system. It is convenient to make a formal splitting of \( V \) into an isotropic part which is independent of the orientations of the molecules,

\[
V_i(\vec{r}_N) = \langle V(\vec{\Omega}_N, \vec{r}_N) \rangle \tag{3.2}
\]

in which the brackets \( \langle \rangle \) denote an unweighted average over all orientations of the molecules, and an anisotropic part,

\[
V_a(\vec{\Omega}_N, \vec{r}_N) = V(\vec{\Omega}_N, \vec{r}_N) - \langle V(\vec{\Omega}_N, \vec{r}_N) \rangle \tag{3.3}
\]
so that\[ V_{(\vec{\omega}_1^N, \vec{\omega}_2^N)} = V_{\omega_1^N} + V_{\omega_2^N} \]

We assume that the anisotropic interaction energy is additive, so that \( V_a \) is given by the sum of contributions from all pairs of molecules in the system. Let us denote the pair interaction energy of molecules 1 and 2 by

\[ V = V_a(\vec{\omega}_1, \vec{\omega}_2, R) + V_{\omega}(R) \quad (3.4) \]

where \( \vec{\omega}_1 \) and \( \vec{\omega}_2 \) denote the orientations of molecules 1 and 2 relative to the intermolecular axis, and \( R \) denotes the separation of their centers of charge. The anisotropic pair potential (3.4) can be expanded in products of spherical harmonics,

\[ V_a(\vec{\omega}_1, \vec{\omega}_2, R) = \sum_{j_1 j_2, m} A_{j_1 j_2 m}(R) Y_{j_1 m}(\vec{\omega}_1) Y_{j_2 m}(\vec{\omega}_2) \quad (3.5) \]

Two cases may arise here:

(i) The anisotropic pair interaction energy (3.5) can be taken to be zero if both molecules are in the \( J=0 \) (ground) rotational state as is the case in this experiment. The potential energy (3.4) between molecules 1 and 2 then becomes

\[ V = V_{\omega}(R) \]

When expressed in terms of coordinates located at the centers of charge, the interaction between two HD molecules is almost identical to that between two \( H_2 \) molecules. This interaction is best represented by a potential of the
\[ V(R) = \xi_2 \exp(-\eta (R-a)/a) - \xi_1 (a/R) \quad (3.6) \]

where \( \xi_1 = 3.7 \text{ cm}^{-1} \), \( \xi_2 = 5 \text{ cm}^{-1} \), \( \eta = 13 \) and \( a = 3.66 \text{ Å} \) are parameters characterizing the molecule pair and \( R \) is the separation between their centers of charge. We assume that the potential for a pair of HD molecules is also given by (3.6) but with a small angle deviation depending on the relative orientation of the molecules because the centers of mass and charge do not coincide in an HD molecule. In Fig. 7 the geometrical quantities characterizing an interacting pair of HD molecules are defined. Following Crane and Gush (16), we express \( R \) in terms of the separation between the centers of mass \( R \) and the orientation \( \hat{\omega}_1, \hat{\omega}_2 \) of the two molecules with respect to \( R \) as polar axis. We see that

\[
\hat{i}_1 = \begin{bmatrix} \sin \theta_1 \cos \phi_1, \sin \theta_1 \sin \phi_1, \cos \theta_1 \end{bmatrix}, \quad \hat{i}_2 = \begin{bmatrix} \sin \theta_2 \cos \phi_2, \sin \theta_2 \sin \phi_2, \cos \theta_2 \end{bmatrix}
\]

\[ \overrightarrow{R} = -\Delta \hat{i}_2 + \overrightarrow{R}_0 + \Delta \hat{i}_1 \]

Forming the scalar product of \( \overrightarrow{R} \) with itself, we get

\[ R^2 = R_0^2 + 2 \Delta (\hat{i}_1 \cdot \overrightarrow{R}_0 - \hat{i}_2 \cdot \overrightarrow{R}_0) - 2 \Delta^2 (\hat{i}_1 \cdot \hat{i}_2) + 2 \Delta^2 \]

Since \( \hat{i}_1 \cdot \hat{i}_2 = \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos (\phi_1 - \phi_2) \), the relation between \( R \) and \( R_0 \) becomes,
Figure 7. Relative orientations of two HD molecules.
ω_i is the orientation of molecule i relative to the axis along the line joining the centers of mass; X-center of mass, ◦-center of charge. Ref.(16)
\[ R = R_0 \left\{ 1 + 2 \left( \frac{\Delta}{R_0} \right) (\cos \theta_1 - \cos \theta_2) \right. \\
+ 2 \left( \frac{\Delta}{R_0} \right)^2 \left[ 1 - \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos (\phi_1 - \phi_2) \right] \right\} \\
= R_0 \left\{ 1 + 2 \left( \frac{\Delta}{R_0} \right)^2 \left[ 1 - \frac{4\pi}{3} \left( \gamma_{10}(\tilde{\omega}_1) - \gamma_{10}(\tilde{\omega}_2) \right) \right] \\
+ 2 \left( \frac{\Delta}{R_0} \right)^2 \left[ 1 - \frac{4\pi}{3} \left( \gamma_{10}(\tilde{\omega}_1) \gamma_{10}(\tilde{\omega}_2) - \gamma_{11}(\tilde{\omega}_1) \gamma_{11}(\tilde{\omega}_2) \right) \\
- \gamma_{11}(\tilde{\omega}_1) \gamma_{11}(\tilde{\omega}_2) \right] \right\} \] (3.7)

where \( \tilde{\omega}_i = (\theta_i, \phi_i) \) and \( i = 1, 2 \). If Eq. (3.7) is substituted into Eq. (3.6) and expanded in terms of \( R_0 \) then the pair potential can be written as

\[ V(R) = V(R_0) + V'(R_0) + A_1(\tilde{\omega}_1, R_0) + A_1(\tilde{\omega}_2, R_0) \]
\[ + A_2(\tilde{\omega}_1, \tilde{\omega}_2, R_0) \] (3.8)

where terms up to the order of \( \left( \frac{\Delta}{R_0} \right)^2 \approx \frac{1}{900} \) are retained. The expansion of the last term in Eq. (3.8) in terms of spherical harmonics takes the form

\[ A_2(\tilde{\omega}_1, \tilde{\omega}_2, R_0) = 4\pi \sum_{m} A_m(R_0) Y_{j,m}(\tilde{\omega}_1) Y_{j,-m}(\tilde{\omega}_2) \] (3.9)

This term couples the rotational motion of two adjacent molecules and is responsible for \( \Delta J = 1 \) transitions in solid HD.

(ii) Suppose for simplicity that the system consists of a single orthohydrogen \((J=1)\) molecule and \( N-1 \) HD \((J=0)\) molecules.
This is the case appropriate to our experimental situation since we have about 7% orthohydrogen impurity in our HD sample. In the approximation that the HD molecules can be regarded as being permanently in their ground rotational states, the anisotropic pair interaction energy (3.5) can be taken to be zero unless one of molecules 1 and 2 is the orthohydrogen molecule in which case,

\[ V(\hat{\omega}', R) = \sum_{j=2}^{\infty} v(R)Y_{j0}(\hat{\omega}') \]  

(3.10)

where \( \hat{\omega}' \) denotes the orientation of the ortho-H\(_2\) molecule relative to the axis joining the center of mass of the ortho-H\(_2\) and the center of charge of the HD molecule. If the ortho-H\(_2\) molecule is in the rotational state \( J=1 \) we need only consider the term \( j=2 \) in Eq.(3.10), since the matrix element of \( Y_{j0}(\hat{\omega}') \) in the rotational subspace \( J=1 \) are identically zero for \( j > 2 \). In any case the terms in (3.10) for which \( j > 2 \) are small compared to the term corresponding to \( j=2 \) and may be neglected so that,

\[ V(\hat{\omega}', R) = v(R)Y_{20}(\hat{\omega}') \]  

(3.11)

where \( v(R) \) is given by Eq.(3.6).

The total anisotropic interaction energy is then obtained by summing the term (3.11) over all the HD molecules in the crystal.

In Fig.8 the geometrical quantities characterizing an interacting pair of H\(_2\) and HD molecules are defined. From Fig.8, we have
Figure 8. Relative orientations of an $\text{H}_2$ and an HD molecules. $
abla_2$ is the orientation of HD molecule relative to the axis along the line joining the centers of mass. $\text{x}$-center of mass, $\Theta$-center of charge.
Expressing the distance between the centers of charge $R$ in terms of the distance between the centers of mass $R_0$ of the $H_2$ and HD molecules, we obtain

$$R = R_0 + \Delta \cos \theta_2$$

Expansion of $v(R)$ to first order in $\Delta$ gives

$$v(R) = v(R_0) + g(R_0)Y_{10}(\hat{\omega}_2)$$

where

$$g(R_0) = \left( \frac{4\pi}{3} \right)^{\frac{1}{2}} \Delta v'(R_0)$$

Substituting Eq. (3.13) into Eq. (3.11), we have

$$V(\hat{\omega}_1', \hat{\omega}_2', R) = v(R_0)Y_{20}(\hat{\omega}_2') + g(R_0)Y_{10}(\hat{\omega}_2)Y_{20}(\hat{\omega}_2')$$

(3.14)

We transform the spherical harmonics to a coordinate system with the $z$-axis along the hexagonal axis of the crystal, giving

$$V(\hat{\omega}_1', \hat{\omega}_2', R_0) = \left( \frac{4\pi}{5} \right)^{\frac{1}{2}} v(R_0) \sum_m Y_{2m}(\hat{\omega}_1)Y_{2m}^*(\beta_1, \alpha_1)$$

$$+ 4\pi \left( \frac{1}{15} \right)^{\frac{1}{2}} g(R_0) \sum_{m, n} Y_{2m}(\hat{\omega}_1)Y_{1m}(\hat{\omega}_2)Y_{2m}(\beta_1, \alpha_1)Y_{1m}(\beta_2, \alpha_2)$$

(3.15)

where $\beta_i$ and $\alpha_i$ ($i = 1, 2$) are the polar angles of $R$ and $R_0$ with respect to the hexagonal axis. Because of the threefold axis of the h.c.p. structure, the terms corresponding to $m =$
\( \pm 1, \pm 2 \) in the first term of (3.15) vanish, and we get

\[
V(\hat{\mathbf{J}_1}, \hat{\mathbf{J}_2}, \mathbf{R}_0) = E_{2c} \left( \frac{4\pi}{3} \right)^{\frac{1}{2}} Y_{20} (\hat{\mathbf{J}_1}) + 4\pi \left( \frac{1}{15} \right)^{\frac{1}{2}} \sum_{m,n} Y_{2m}(\mathbf{R}_1)Y_{1n}(\hat{\mathbf{J}_2})Y_{2m}(\hat{\mathbf{R}})Y_{1n}(\hat{\mathbf{R}_0})
\]

Where the crystalline field constant, \( E_{2c} \), is given by

\[
E_{2c} = V(\mathbf{R}_0)Y_{20}^*(\hat{\mathbf{R}})
\]

and \( Y_{2m}(\hat{\mathbf{R}}) \equiv Y_{2m}(\beta_1, \alpha_1) \), \( Y_{1n}(\hat{\mathbf{R}_0}) \equiv Y_{1n}(\beta_2, \alpha_2) \).

The second term in Eq. (3.16) is the interaction term between the HD and the \( \text{H}_2 \) molecules and is responsible for the quadrupolar induction effect.

The sum of (3.17) over the first two shells of neighbors vanishes, and the contributions from the remaining shells are small and tend to alternate in sign. Consequently, in an h.c.p. lattice vanishes for all practical purposes.

**III.2 Rotational Waves in the J=0 lattice of HD solid**

In considering the pure rotational part of the spectrum, it is convenient to neglect the lattice vibrations and assume that the centers of mass of the molecules are held fixed at the sites of a rigid lattice. The crystal structure of solid HD is hexagonal close-packed (h.c.p.), being built up of alternate layers of \( \alpha- \) and \( \beta- \)planes as shown in Fig. 8. The unit cell contains two molecules and is
Figure 9. Hexagonal Close-packed crystal structure.

α- molecule

β- molecule
formed by the following set of vectors:

\[ \hat{t}_1 = \frac{1}{2} a (\sqrt{3} \hat{i} - \hat{j}) \]
\[ \hat{t}_2 = \frac{1}{2} a (\sqrt{3} \hat{i} + \hat{j}) \]
\[ \hat{t}_3 = \left( \frac{8}{3} \right)^{1/2} \hat{k} = \hat{c} \]

where \(a\) is the nearest neighbor distance. If \( \hat{R}_L \) is the position vector of the \( \alpha \)-molecule in the \(i\)-th unit cell then \( \hat{R}_L + \hat{c} \) is the position vector of the \( \beta \)-molecule in this unit cell. In general, we may write for the lattice vectors

\[ \hat{R}_{i} = \hat{R}_L + \hat{t}_Y \]

where \( Y = \alpha, \beta \) and \( \hat{t}_\alpha = 0, \hat{t}_\beta = \hat{c} \).

At the temperature of solid HD, the molecules are permanently in the ground electronic and ground vibrational states so that the HD crystal is completely described by a wavefunction,

\[ |0,0> = \prod_{j=1}^{N} Y_{\alpha\alpha}(\hat{\Delta}_j) \]

where \( \hat{\Delta}_j \) denotes the orientation of the \( j \)-th molecule referred to the hexagonal axis as the polar axis. The Hamiltonian for the system is

\[ H = -\frac{\hbar^2}{2\mu} \sum_{j=1}^{N} \nabla_j^2 + V(\hat{D}_j; \hat{R}) = T + V_L + V_A \]

where \( V_L \) and \( V_A \) are the total potentials for isotropic and anisotropic forces respectively.
As mentioned in Chapter I, the rotational motion of the molecules in solid HD is nearly free. When we neglect the anisotropic forces (i.e. put $V=0$) the rotations of the molecules are completely unhindered. The wave equation is

$$(\mathbf{T} + V_\perp)|0,0\rangle = E|0,0\rangle$$

and since $V_\perp$ has no dependence on the orientations of the molecules, it is a constant operator and the wave equation becomes

$$T|0,0\rangle = [E - E(0)]|0,0\rangle \quad (3.20)$$

where $E(0)$, the eigenvalue of $V_\perp$, is the energy of the rigid lattice. A particular solution of Eq.(3.20) is

$$|J_j m_j\rangle = \prod_{j=1}^{N} y_j m_j (\hat{J}_j)$$

and the corresponding energy of the crystal is

$$E = E(0) + B \sum_{i=1}^{J} (J_i + 1) + \sum_{i=1}^{N} B J_{iN} (J_{iN} + 1)$$

where $J = 0, 1, 2, \ldots$; $m = 0, \pm 1, \ldots, \pm J$; $i = 1, 2, \ldots, N$ and $B = 44.67 \text{ cm}^{-1}$ (1) is the rotational constant for HD.

The ground state is the state in which all of the molecules are in the $J=0$ state,

$$|00\rangle = \prod_{j=1}^{N} y_{00} (\hat{J}_j)$$

and $E = E(0)$.
This state is non-degenerate. The single exciton state is a state in which a particular molecule, say the molecule at $\vec{R}_{i\ell}$, is in a rotational state $J$, while all of the other molecules are in the rotational state $J=0$.

$$|Jm,\vec{R}_{i\ell}\rangle = Y_{jm}(\vec{J}_{i\ell}) \prod_{j\neq \ell} Y_{0\langle}(\vec{J}_{j\ell})$$

and

$$E = E(0) + BJ(J+1)$$

This state is $(2J+1)N$-fold degenerate since the localized rotational excitation can be located on any one of the $N$ molecules in the crystal and the factor $2J+1$ corresponds to spatial degeneracy. This state is characterized by a wave vector $\vec{k}$ due to translational invariance and must be of the Bloch form.

The double exciton state is a state in which two particular molecules, say those at $\vec{R}_{i\ell}$ and $\vec{R}_{i'\ell'}$, are in excited rotational states $J$ and $J'$, while all the other molecules are in the ground rotational state.

$$|Jm, J'm',\vec{R}_{i\ell}, \vec{R}_{i'\ell'}\rangle = Y_{jm}(\vec{J}_{i\ell}) Y_{j'm'}(\vec{J}_{i'\ell'}) \prod_{j\neq \ell, j' \neq \ell'} Y_{0\langle}(\vec{J}_{j\ell'})$$

and

$$E = E(0) + J(J+1)B + J'(J'+1)B$$

This state is $(2J+1)(2J'+1)N(N+1)/2$-fold degenerate, since the two localized rotational excitations can be located on any distinct pair of molecules in the crystal and the factor $(2J+1)(2J'+1)$ corresponds to spatial degeneracy as before.
When we introduce the anisotropic interaction $V_a$ as a perturbation we shall see that the initially localized rotational excitations do not remain localized but begin travelling through the lattice. The perturbed wave equation is

$$H |\tilde{\Omega}^N\rangle = E |\tilde{\Omega}^N\rangle$$

Let us consider the single exciton state. The wave function describing this state is a linear combination of the $(2J+1)N$ unperturbed wave functions

$$|\tilde{\Omega}^N\rangle = \sum_{\gamma} \sum_{m=-J}^{J} U_m(\mathbf{R}_{\gamma \beta}) |Jm, \mathbf{R}_{\gamma \beta}\rangle$$  \hspace{1cm} (3.21)

Substituting this wave function in the perturbed wave equation, then multiplying by $\langle Jm', R_{\gamma' \beta'} |$ and integrating over $\tilde{\Omega}^N$, we get

$$\sum_{\gamma'} \sum_{Jn} \langle Jm', R_{\gamma' \beta'} | H |Jm, \mathbf{R}_{\gamma \beta}\rangle U_n(\mathbf{R}_{\gamma' \beta'}) = EU_m(\mathbf{R}_{\gamma \beta})$$  \hspace{1cm} (3.22)

Now the quantity $U_m(\mathbf{R}_{\gamma \beta})$, as can be seen from Eq.(3.21), is equal to the probability amplitude of finding the crystal in the state $|Jm, R_{\gamma \beta}\rangle$, i.e. of finding the rotational exciton at $\mathbf{R}_{\gamma \beta}$ and with a $Z$-component of "spin" equal to $m$. The coefficients $U_m(\mathbf{R}_{\gamma \beta})$ can therefore be regarded as the wave functions describing the motion of the exciton through the lattice and the precessional motion of its spin. Because of the existence of an inversion center between the $\alpha$ and $\beta$ sites, linear combinations of the basic functions given by Eq.(3.22) can be written down such that they form even or
odd-parity states under inversion giving the symmetrized Bloch states

\[ |m, p\rangle = N^{-\frac{1}{2}} \sum_{i=1}^{N_0} e^{-i\mathbf{k} \cdot \mathbf{R}_i} \left[ |Jm, R_{i\alpha}\rangle + \phi |Jm, \mathbf{R}_{i\beta}\rangle \right] \]

where \( m \) is the projection of the \( J \) on the crystal \( c \)-axis, \( \mathbf{k} \) is the wave vector of the rotational exciton, \( N_0 = \frac{1}{2} N \) is the number of unit cells and \( p = \pm \). In particular when \( k = 0 \), the "+" refers to the two molecules in each unit cell rotating in phase, and "-" to these molecules rotating in anti-phase.

Since the potential in the crystal is periodic, the solutions of Eq.(3.22) will take the form

\[ U_m(\mathbf{R}, \mathbf{y}) = A_{m,\gamma}(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{R}} \]

where the amplitudes are the solutions of the 10X10 secular equation

\[ \sum_{m', y'} H_{m, m', y'}(\mathbf{k}) A_{m', y'}(\mathbf{k}) = E(\mathbf{k}) A_{m, y}(\mathbf{k}) \]

The Hamiltonian matrix is given by

\[ H_{m, m', y'}(\mathbf{k}) = \sum_j \langle Jm, R_{i\gamma} | H | Jm', R_{i\delta} \rangle e^{i\mathbf{k} \cdot (\mathbf{R}_{i\delta} - \mathbf{R}_{i\gamma})} \]  

(3.23)

In particular, for \( J=2 \) band, the main anisotropic force between the HD molecules is the electric quadrupole quadrupole (EQQ) force (23). Neglecting all other anisotropic interactions, we obtain from Eq.(3.23) and Ref.(24),
where $^\text{mm}T(-1)C(224; m', -m')$ and the lattice sums $S^{y'z'}_m(k)$ are defined by

$$S^{\alpha\beta}_m(k) = S^{\omega\beta}_{m' m}(-k) = \sum_{\rho} (a/R_\rho)^5 \gamma_{4, m', m}^*(\vec{\Omega}_\rho) e^{i\vec{k} \cdot \vec{R}_\rho}$$

The sum in Eq. (3.25) extends over all the $\alpha$ neighbors of the central molecule. The sum in Eq. (3.16) includes the origin, and $R_{\alpha\beta}$ runs over the vectors extending from the central molecule to all the $\beta$ molecules. This is the model we will use for the rotational waves in the solid HD lattice.
III.3 Multipole Moments Induced Dipole Moment

Consider two rigid, non-overlapping charge distributions 1 and 2, of arbitrary shape, centered around origins $O_1$ and $O_2$ in a space fixed frame 0. The multipole components of the charge distribution 2 are defined by

$$Q_{jm} = \int \bar{r} \rho(\bar{r}) r^i Y_{jm}^* (\bar{r})$$

where the integration extends over all the charges in the distribution, and $\bar{r} = (r, \theta, \phi) = (r, \theta, \phi)$ is the position of the charge density $\rho(\bar{r})$ relative to the origin of the distribution in the space fixed frame 0. The $Q_{jm}$ are the components of an irreducible tensor of rank $j$. The potential at charge 1 due to the electric multipole moments of the charge distribution 2 is,

$$\Phi_j = \frac{4\pi}{2j+1} \sum_m Q_{jm}^* \frac{Y_{jm}(\bar{r})}{R^{j+1}}$$

where $Q_{jm}^*$ is the complex conjugate of $Q_{jm}$ and $R$ is the distance between the two charge centers.

The dipole moment $\vec{\mu}$ induced in charge 1 by the multipole moments of charge 2 is,

$$\vec{\mu} = p\vec{E} = p(-\nabla \Phi_j)$$

$$= \frac{4\pi}{2j+1} \sum_m Q_{jm}^* p \frac{Y_{jm}(\bar{r})}{R^{j+1}}$$

where $\vec{E}$ is the electric field at 1 due to 2.
Introducing the spherical basis vectors

\[ \vec{e}_z = \frac{1}{\sqrt{2}}(\hat{e}_x + i\hat{e}_y) \]

\[ \vec{e}_0 = \hat{e}_z \]

where \( \hat{e}_x, \hat{e}_y, \) and \( \hat{e}_z \) are unit vectors along the space fixed Cartesian coordinate axes, the spherical components of \( \vec{\mu} \) are

\[ \mu_\nu = \vec{\mu} \cdot \vec{e}_\nu = -\frac{4\pi}{2j+1} p \sum_m q_{j,m}^* \frac{Y_{j,m}(\vec{r})}{R^{j+1}} \]

(3.30)

where \( \nu = 0, \pm 1 \).

Using the gradient formula derived by Rose (25), we have

\[ \nabla_\nu \Phi(R) Y_{j,m}(\vec{r}) = \frac{j+1}{2j+3} C(j,l,j+l;m,\nu) Y_{j+1,m+l} (\vec{r}) (\frac{d\Phi}{dR} - \frac{j}{R} \Phi) \]

\[ -\frac{j}{2j+1} C(j,l,j-1;m,\nu) Y_{j-1,m+l} (\vec{r}) (\frac{d\Phi}{dR} + \frac{j+1}{R} \Phi) \]

(3.31)

Since

\[ \frac{d\Phi}{dR} + \frac{j+1}{R} \Phi = 0 \]

and

\[ \frac{d\Phi}{dR} - \frac{j}{R} \Phi = -\frac{2j+1}{R^{j+2}} \]

we find from Eqs. (3.30) and (3.31) the induced dipole moment in charge 1 has the following expression

\[ \mu_\nu = 4\pi \sqrt{\frac{j+1}{2j+3}} p \sum_m C(j,l,j+l;m,\nu,m+\nu) Y_{l+1,m+l} (\vec{r}) q_{j,m}^* \frac{1}{R^{j+1}} \]

(3.32)

where \( \nu = 0, \pm 1 \).

We will use this equation to derive expressions of integrated absorption coefficient for the zero phonon rotational transitions in the next section.
III.4 The Zero Phonon Rotational Transitions

(i) $V_{\omega \rightarrow 0}(0)$ transitions

The $V(\Delta J=5)$ transitions arise from the 32($=2^5$)-polar induced dipole moment. In what follows in this subsection, a rigid h.c.p. lattice structure for solid HD is assumed. Consider a single crystal of HD. Let the hexagonal axis coincide with the Z-axis of a space fixed XYZ frame, whose origin coincides with the center of charge of molecule 0 in the crystal. The spherical component of the dipole moment induced in molecule $k$ by the multipole field of molecule 0 is from Eq. (3.32)

$$\mu_j^k = 4\pi \left( \frac{j+1}{2j+1} \right) \rho \sum_m C(j,1,j+1;\nu,m+\nu) Q_{jm}^* (0) \frac{Y_{j+1,m+\nu}(\Omega_k)}{R_k^{j+2}}$$ (3.33)

Here $\rho$ is the isotropic polarizability; $Q_{jm}^*$ is the $m$-th spherical component of the $j$-th multipole moment in the space fixed frame; $Y_{jm}$ is a spherical harmonics, $\Omega_k$ represents the angular coordinates ($\theta_k, \phi_k$) of molecule $k$, $R_k$ is the distance from the center of charge of molecule $k$ to the center of charge of the molecule at the origin 0 and $C(j,1,j+1;\nu,m,\nu,m+\nu)$ are Clebsch-Gordan coefficients. If we let $Q_{jn}$ stand for the components of the multipole moment in the molecule fixed frame $x, y, z$, with $z$-axis along the molecular axis, the inherent cylindrical symmetry of the problem implies that $\overline{Q}_{jn} = \overline{Q}_{j0} \delta_{n0}$. Also $\overline{Q}_{jn}$ and $Q_{jm}$ are connected by
\[ Q_{jm} = \sum_{n} D_{mn}^{*}(\Omega_{0})\overline{Q}_{jn} = D_{m0}^{*}(\Omega_{0})\overline{Q}_{j0} \]  

(3.34)

Here \( D_{mn} \) is a rotation matrix and \( \overline{Q}_{j0} \) is the orientation of the \( xyz \) frame with respect to the \( XYZ \) frame. From Rose (26), we note that

\[ D_{m0}^{*}(\Omega_{0}) = \left( \frac{4\pi}{2j+1} \right)^{1/2} Y_{jm}(\Omega_{0}) \]  

(3.35)

Following Gray (14), we define the scalar magnitude of the \( j \)-th multipole moment by

\[ Q_{j}^{2} = \frac{4\pi}{2j+1} \sum_{n} |\overline{Q}_{jn}|^{2} = \frac{4\pi}{2j+1} \overline{Q}_{j0}^{2} \]  

(3.36)

In view of equations (3.34) through (3.36), Eq.(3.33) becomes

\[ \mu_{V}^{k} = 4\pi \frac{(j+1)}{2j+3} \overline{Q} \sum_{m} C(j, l, j+1; m, \nu, m+\nu) Y_{jm}^{*}(\overline{\Omega}_{0}) Y_{j+1, m+\nu}(\overline{\Omega}_{k}) \]  

(3.37)

where \( \overline{\Omega}_{0} \) and \( \overline{\Omega}_{k} \) represent the orientations of the molecule 0 at the origin and molecule \( k \) in the h.c.p. lattice with respect to the space fixed frame \( XYZ \) respectively. As stated above, the \( V \) transitions occur due to the 32-polar induced dipole moment and we therefore, specialize for the case \( j=5 \). Eq.(3.37) now becomes

\[ \mu_{V}^{k} = 4\pi \frac{(5)}{13} \overline{Q} \sum_{m} C(5, l, 6; m, \nu, m+\nu) Y_{5m}^{*}(\overline{\Omega}_{0}) Y_{6, m+\nu}(\overline{\Omega}_{k}) \]  

(3.38)

The total induced dipole moment obtained by summing
contributions from all lattice points (except molecule 0 itself) becomes

\[ \mu_v = \sum_k \mu_v^k \]

\[ = 4\pi \left( \frac{6}{13} \right)^{\frac{1}{2}} \frac{pQ_s}{\alpha^2} \sum_m C(5,1,6; m, \nu, m+\nu) y_5^* (\tilde{m}^0_0) \sum_k \left( \frac{a}{R_k^0} \right) y_6, m+\nu (\tilde{m}^0_k) \]

(3.39)

Since HD is a heteronuclear molecule, the center of mass (CM) does not coincide with the center of charge (CG). The 32-pole moment is defined in the CG coordinates, while the rotational motion is defined in the CM coordinates as is done in Section 2. Gray (27) has shown the transformation formula to be as follows:

\[ Q_j' = Q_j + \sum_{j=0}^{l-1} \left( \frac{(-1)^{j-j_1}}{j_1! (j-j_1)!} \right) \Delta^{j-j_1} Q_j \]

(3.40)

where \( Q_j' \) is the multipole moment in CM coordinates, \( Q_j \) is the multipole moment in CG coordinates, and \( \Delta \) is the distance between the two origins (in HD \( \Delta = 0.1236 \) Å).

Applying Eq.(3.40), we have

\[ Q_5' = Q_5 + (-5)\Delta Q_4 + 10\Delta^2 Q_3 + (-1)^{10} \Delta^3 Q_2 + 5\Delta^4 Q \]

(3.41)

We note that in the CG coordinates all odd order multipole moments vanish except a weak oscillating electric dipole moment \( Q_1 \), which may be neglected in first approximation.

Eq.(3.41) becomes
The transformation of spherical harmonics is a formidable task and will not be attempted here. The transformation of the distance $R'$ between centers of charge to the distance $R$ between the centers of mass is given by Eq. (3.7) as

$$R' = R \left\{ 1 + 2 \frac{4\pi}{3} \frac{\Delta}{R} \left[ Y_{10}(\vec{r}_0) - Y_{10}(\vec{r}_0') \right] \right\}^{1/2}$$

if terms up to the first order in $\frac{\Delta}{R} \sim \frac{1}{10}$ are kept. But the transformed term linear in $\Delta$ has no nonvanishing matrix elements between the initial $|0,0>$ and final $|5,M'>$ states of the central molecule. In first approximation, we may assume a 32-pole moment of magnitude given by Eq. (3.42) exists in the CM coordinates and consider all the coordinates appearing in Eq. (3.39) as measured in the CM frame. With this in mind, Eq. (3.39) becomes

$$\mu_\nu = A \sum_m C(5,1,6;m,\nu m+\nu)Y_{5,m}^*(\vec{r}_0) \sum_k \left( \frac{a}{R_k} \right) Y_{6,m+\nu} (\vec{r}_k)$$  (3.43)

where $A = 4\pi^2 Q_4 / a^3$ and $\vec{r}_0, \vec{r}_k$ are the orientations in the CM coordinates of the central molecule and molecule $k$ respectively with the hexagonal axis as polar axis.

We define the lattice sum $S$ as follows

$$S = \sum_k \left( \frac{a}{R_k} \right)^{1/2} Y_{6,m+\nu} (\vec{r}_k)$$  (3.44)

It is shown in Appendix A that by applying the symmetry arguments appropriate to an h.c.p. lattice, the lattice sum

$$Q_5' = -5\Delta Q_4 - 10\Delta^3 Q_2$$  (3.42)
(3.44) is non-zero only for \( m+v = 0 \) or \( \pm 6 \) and that \( S \) may be taken to be real which has the same value for both \( m+v = 0 \) and \( m+v = 6 \) or \( -6 \). By virtue of this, Eq. (3.43) becomes

\[
\mu_v = A \sum_{m} C(5,1,6; m, -m, 0) Y_{5,m}^* (\vec{\Omega}_0) \delta_{m,-v} \sum_k \left( \frac{a}{R_k} \right)^7 Y_{6,0} (\vec{\Omega}_k) + C(5,1,6; m, 6-m, 6) Y_{5,m}^* (\vec{\Omega}_0) \delta_{m,6-v} \sum_k \left( \frac{a}{R_k} \right)^7 Y_{6,-6} (\vec{\Omega}_k)
\]

Eq. (3.45) now becomes

\[
\mu_v = A \left[ \frac{1}{15} S_1 \left( \frac{13}{4\pi} \right) \right]^{1/2} \left[ C(5,1,6; -v, v, 0) Y_{5,-v}^* (\vec{\Omega}_0) \right] + \left( \frac{3003}{4096} \right)^{1/2} S_2 \left[ C(5,1,6; 6-v, v, 6) Y_{5,6-v}^* (\vec{\Omega}_0) \right] + C(5,1,6; -6-v, v, -6) Y_{5,-6-v}^* (\vec{\Omega}_0)
\]

We define the lattice sums \( S_1 \) and \( S_2 \) as

\[
S_1 = \sum_k \left( \frac{a}{R_k} \right)^7 \{ 231 \cos^6 \theta - 315 \cos^4 \theta + 105 \cos^2 \theta - 5 \}
\]

\[
S_2 = \sum_k \left( \frac{a}{R_k} \right)^7 \sin \theta e^{i\phi}
\]

The rapidly convergent sums \( S_1 \) and \( S_2 \) have the following values (28)

\[
S_1 = -67.59024
\]

\[
S_2 = 5.5825
\]

Eq. (3.45) now becomes

\[
\mu_v = A \left[ \frac{1}{15} S_1 \left( \frac{13}{4\pi} \right) \right]^{1/2} \left[ C(5,1,6; -v, v, 0) Y_{5,-v}^* (\vec{\Omega}_0) \right] + \left( \frac{3003}{4096} \right)^{1/2} S_2 \left[ C(5,1,6; 6-v, v, 6) Y_{5,6-v}^* (\vec{\Omega}_0) \right] + C(5,1,6; -6-v, v, -6) Y_{5,-6-v}^* (\vec{\Omega}_0)
\]

In an HD crystal at 0°K all the molecules are in the \( J=0 \) rotational state. Due to the occurrence of \( Y_{5,m}^* (\vec{\Omega}_0) \) in
Eq. (3.46) for the total induced dipole moment, transitions in which molecule 0 is lifted to \( J=5 \) states are possible. Assuming this excitation to be localized, the transition matrix elements of \( \mu_\nu \) between the initial state \( Y_{0,0}(\vec{r}_0) \) and the final state \( Y_{5,m}(\vec{r}_0) \) are given by

\[
\mu_\nu^{0M'} = \langle 0,0 | \mu_\nu | 5,M' \rangle
\]  

(3.47)

Here we define \( \mu_\nu^{M'M'} \) as

\[
\mu_\nu^{M'M'} = \langle J'M' | \mu_\nu | J'M' \rangle
\]

where we indicate quantities associated with the upper state by a single prime mark ('') and those associated with the lower state by two prime marks ("'). Now for the spherical component \( \mu_0 \), the last two terms involving the sum \( S_2 \) in Eq. (3.46) add to zero. Eq. (3.47) becomes

\[
\mu_0^{0M'} = \langle 0,0 | \mu_0 | 5,M' \rangle
= \frac{1}{16} \left( \frac{11}{14} \right)^{1/2} S_1 C(5,1,6;0,0,0) \langle Y_{0,0} | Y_{5,0} | Y_{5,M'} \rangle \delta_{0,M'}
\]

(3.48)

Similarly

\[
\mu_1^{0M'} = \langle 0,0 | \mu_1 | 5,M' \rangle
= \frac{1}{16} \left( \frac{11}{14} \right)^{1/2} S_1 C(5,1,6;1,0,0) \langle Y_{0,0} | Y_{5,-1} | Y_{5,M'} \rangle \delta_{M',1}
+ \frac{3 \cdot 9 \cdot 3}{4 \cdot 0 \cdot 5 \cdot 6} \left( \frac{11}{14} \right)^{1/2} S_2 C(5,1,6;5,1,6) \langle Y_{0,0} | Y_{5,5} | Y_{5,M'} \rangle \delta_{M',5}
\]

(3.49)
The Clebsch-Gordan coefficients appearing in equations (3.48) through (3.50) have the following values

\[ C(5,1,6;0,0,0) = \left(\frac{1}{11}\right)^{1/2} \]

\[ C(5,1,6;-1,1,0) = C(5,1,6;1,-1,0) = \left(\frac{5}{22}\right)^{1/2} \]  

and \[ C(5,1,6;5,1,6) = C(5,1,6;-5,-1,-6) = 1 \]

From equations (3.48) through (3.51) we finally obtain

\[ \mu_0 = \alpha S_1 \left(\frac{1}{12}, \frac{13}{14}, \frac{6}{11}\right)^{1/2} \frac{1}{16} \]

\[ \mu_1^{-1} = \mu_1^0 = \alpha S_1 \left(\frac{1}{12}, \frac{13}{14}, \frac{5}{22}\right)^{1/2} \]

\[ \mu_1^{05} = \mu_1^{-5} = \alpha S_2 \left(\frac{1}{4\pi}, \frac{3003}{4096}\right)^{1/2} \frac{1}{16} \]

This shows that only the sublevels \( M' = 0, \pm 1 \) and \( \pm 5 \) are accessible by infrared absorption. Sublevels \( M' = \pm 2, \pm 3, \pm 4 \) are inactive.

The integrated absorption coefficient \( \mu \) is given by Herzberg (29) as
From Eq. (3.52) we obtain

\[ \tilde{\alpha} = \frac{8\pi^3}{3h} \sum_{M'M'\nu} \left| \mu_{\nu}^{M'M'} \right|^2 \]  

(3.52)

From Eq. (3.52) we obtain

\[ \tilde{\alpha} [V_\nu(0)] = \frac{816.7\pi^3}{16} \frac{p^2 Q_5^2}{a^{14} h} \]  

(3.53)

where \( Q_5' \) is the rovibrational matrix element \( \langle 0,0|Q_5'|\nu,5 \rangle \) of the 32-pole moment; \( h \) is the Planck's constant; and \( a \) is the nearest neighbor distance.

Since quadrupole and hexadecapole moments of HD are unknown at present, corresponding values of \( \text{H}_2 \) are used (30). Applying Eq. (3.42) we find \( Q_5' = -0.4554 \) a.u. (atomic units). By using \( p = 5.414 \) a.u. (31) and \( a = 3.66 \) Å (32) in Eq. (3.53) we find the integrated absorption coefficient for the pure rotational \( V \) transition as

\[ \tilde{\alpha} [V_0(0)] = 1.29 \times 10^{-16} \text{ cm}^3/\text{sec} \]

The present method has distinct advantage in that the infrared activity of individual \( 2M'+1 \) sublevels have been automatically included in the derivation. This information is useful if one wants to study the absorption with polarized light in a single crystal.

(ii) \( U_{\nu-0}(0) \) transitions
The $U(\Delta J=4)$ transitions arise from the hexadecapolar induced dipole moment, which has the following expression

$$\mu_{\nu} = \sum_k \mu_{\nu}^k$$

$$= 4n \left( \frac{s}{14} \right)^{1/2} P Q^4 a^6 \ C(4,1,5; m, \nu, m+\nu) Y_{4,m}(\Omega_0) \sum_k \left( \frac{a}{R_k} \right)^6 Y_{5,m+\nu}(\hat{\Omega}_k)$$

(3.54)

where $Q_k, R_k, \Omega_0$ and $\hat{\Omega}_k$ are understood to be the corresponding quantities in the CM coordinates.

The lattice sum $S'$ is defined as follows,

$$S' = \sum_k \left( \frac{a}{R_k} \right)^6 Y_{5,m+\nu}(\hat{\Omega}_k)$$

(3.55)

$\mu_{\nu}$ is non-zero only for $m+\nu = 3$ or $-3$ after applying the symmetry operation appropriate to an h.c.p. lattice. As a result of this simplification the lattice sum reduces to $S'$

$$= \frac{1}{32} \sqrt{\frac{770}{2\pi}} S$$

where

$$S = \sum_k \left( \frac{a}{R_k} \right)^6 \sin^3 \theta_k (9 \cos^2 \theta_k - 1) e^{i 3 \phi_k}$$

(3.56)

which has the value $5.11053 (28)$ after summing over the whole lattice. Eq. (3.54) now becomes

$$\mu_{\nu} = AS C(4,1,5; 3-\nu, \nu, 3) Y_{4,3-\nu}(\Omega_0)$$

$$+ C(4,1,5; -3-\nu, \nu, -3) Y_{4,-3-\nu}(\hat{\Omega}_k)$$

(3.57)

where $A = \left( \frac{175}{64} \right)^{1/2} P Q^4 / a^6$

The transition matrix elements of $\mu_{\nu}$ between the initial state $Y_{0,0}(\Omega_0)$ and the final state $Y_{4,m}(\Omega_0)$ are given
by

\[ \mu_{M'}^{0} = \langle 0,0 | \mu_{M'} | 4,M' \rangle \]

From Eq. (3.57) we obtain

\[ \mu_{0,3}^{0} = \mu_{0,-3}^{0} = AS \left( \frac{1}{4\pi} \right)^{\frac{1}{2}} \left( \frac{16}{45} \right)^{\frac{1}{2}} \]
\[ \mu_{1,1}^{0} = \mu_{1,-1}^{0} = AS \left( \frac{1}{4\pi} \right)^{\frac{1}{2}} \left( \frac{28}{45} \right)^{\frac{1}{2}} \]
\[ \mu_{1,1}^{0,-4} = \mu_{1,-1}^{0,4} = AS \left( \frac{1}{4\pi} \right)^{\frac{1}{2}} \left( \frac{1}{45} \right)^{\frac{1}{2}} \] (3.58)

This shows that only the sublevels \( M' = \pm 2, \pm 3, \pm 4 \) are accessible by infrared absorption. The levels \( M' = 0, \pm 1 \) are inactive. From Eq. (3.52) we obtain

\[ \alpha \left[ U_{v=0}(0) \right] = \frac{175}{48} \pi^{3} \frac{Q_{4}^{2}p^{2}S^{2}}{h_{a}^{12}} \] (3.59)

where \( Q_{4} \) is the appropriate rovibrational matrix element of the hexadecapole moment \( \langle 0,0 | Q_{4} | v,4 \rangle \).

Applying Eq. (3.40) and using \( H_{2} \) values for those parameters that are unknown for HD, we find \( Q_{4} = 0.5058 \) a.u. and \( \alpha \left[ U_{0}(0) \right] = 1.5 \times 10^{-15} \) cm\(^3\)/sec for the pure rotational \( U \) transition.

(iii) \( T_{v=0}(0) \) transitions

The \( T(\Delta J=3) \) transitions arise due to the octupolar\((2^{3})\) induced dipole moment in the molecule making the transition. The total induced dipole moment at the molecule at the
origin 0 is from Eq.(3.41) as

\[ \mu_\nu = \frac{8\pi DQ_3}{a^5} \sum_m C(3,1,4;\nu,\nu,\nu+1) \psi_{3,m}(\hat{\Omega}_0) S' \]  

(3.60)

where the lattice sum is defined as

\[ S' = \sum_k \left( \frac{a}{R_k} \right)^5 \psi_{4,m+\nu}(\hat{\Omega}_k) \]  

(3.61)

After the symmetry operations the lattice sum \( S' \) reduces to

\[ S' = \frac{3}{16} \left( \frac{1}{2} \right)^{1/2} \sum_k \left( 35 \cos^4 \theta_k - 30 \cos^2 \theta_k + 3 \right) \left( \frac{a}{R_k} \right)^5 \]

\[ = \frac{3}{16} \left( \frac{1}{2} \right)^{1/2} S \]  

(3.62)

where the lattice sum \( S = \sum_k \left( 35 \cos^4 \theta_k - 30 \cos^2 \theta_k + 3 \right) \left( \frac{a}{R_k} \right)^5 \) has the value 5.7709 (28) after summing over the whole h.c.p. lattice. With this simplification Eq.(3.60) becomes

\[ \mu_\nu = ASC(3,1,4;\nu,\nu,0) \psi_{3,\nu}(\hat{\Omega}_0) \]  

(3.63)

where \( A = \frac{\pi}{2} DQ_3/a^5 \).

The non-vanishing matrix elements of \( \mu_\nu \) are

\[ \mu^{0,M''}_{\nu} = \langle 0,0 | \mu_\nu | 3,M'' \rangle \]

From Eq.(3.63), we obtain

\[ \mu^{0,0}_0 = AS \left( \frac{1}{17\pi} \right)^{1/2} \]

\[ \mu^{0,\pm1}_0 = AS/2 \left( \frac{3}{14\pi} \right)^{1/2} \]  

(3.64)

This shows that only the sublevels \( M'' = 0,\pm1 \) are accessible by infrared absorption. The levels \( M'' = \pm2, \pm3 \) are inactive.

From Eq.(3.52) we obtain
where $Q_3$ is the rovibrational matrix element of the octupole moment $<0,0 | Q_3 | v,3>$. Applying Eq. (3.40), we have

$$Q_3 = -3Q_2\Delta + 3Q_1\Delta^2$$

Using $Q_1 = 5.85 \times 10^{-4} \text{ D (1D = } 10^{-18} \text{ e.s.u.}) (33)$ and $p = 5.414 \text{ a.u.}$, we find $\alpha[T_0(0)] = 1.58 \times 10^{-15} \text{ cm}^3/\text{sec}$ for the pure rotational $T$ transition.

### III.5 Zero Phonon $R(\Delta J=1)$ Transitions

(i) The single $R_{1\rightarrow 0}(0)$ transition

The pair dipole moment for $H_2$ molecules 1 and 2, corresponding to molecule 1 making a vibrational transition, is given by

$$M_v(\vec{\omega}_1, \vec{\omega}_2; R) = 4\pi \sum_{\lambda_1,\lambda_2,\mu_1,\mu_2} \mathcal{D}_v(\lambda_1, \mu_1, \lambda_2, \mu_2; R) Y_{\lambda_1, \mu_1}(\vec{\omega}_1) Y_{\lambda_2, \mu_2}(\vec{\omega}_2)$$

$$\alpha[T_v(0)] = \frac{\pi^3}{6} \frac{Q_3^2 \phi S^2}{\hbar Q_1^\nu}$$

where $\nu=0,\pm 1$ refers to the spherical components and $\vec{\omega}_v$ are the orientation angles of the molecules relative to the intermolecular axis $R$. The important nonvanishing coefficients are (34)

$$D_0(0000) = \xi e^{-R/\rho}$$

$$D_0(2000) = \frac{3}{\sqrt{15}} \frac{Q' \phi}{R^4}, \quad D_0(2\pm100) = -\frac{3}{\sqrt{15}} \frac{Q' \phi}{R^4}$$
The coefficient $D_0(0000)$ arises from the overlap induction effect, where $\xi$ and $\rho$ are parameters describing the strength and the range of the dipole moment. The other six coefficients arise from the quadrupolar induction effect. $Q$ and $p$ are the quadrupole moments and polarisabilities of the molecules, with primes to denote the derivatives of the quantities with respect to the intermolecular separation of molecule 1 which undergoes the vibrational transition.

Although $R$ is the distance between the centers of charge, it is also the separation between the centers of mass for a pair of $H_2$ molecules. However, in an HD molecule these are separated by an amount $\Delta=0.123$ Å. We expand $R$ in Eq.(3.67) in terms of $R_0$ as in Eq.(3.7) and keep only terms up to the first order in $\Delta/R_0 \sim 1/30$. We get the following terms

\[
D_0(0000) = \xi e^{-\frac{R_0}{\rho}} - \xi e^{-\frac{R_0}{\rho}} \frac{\Delta}{\rho} \frac{4\pi}{3} [Y_{10}(\overline{w}_1) - Y_{10}(\overline{w}_2)]
\]

\[
D_0(0200) = \frac{3}{\sqrt{5}} \frac{Q'p}{R_0^4} - 12\Delta \frac{4\pi}{\sqrt{15}} \frac{Q'p}{R_0^5} [Y_{10}(\overline{w}_1) - Y_{10}(\overline{w}_2)]
\]

\[
D_0(0020) = -\frac{3}{\sqrt{5}} \frac{Q'p}{R_0^4} + 12\Delta \frac{4\pi}{\sqrt{15}} \frac{Q'p}{R_0^5} [Y_{10}(\overline{w}_1) - Y_{10}(\overline{w}_2)]
\]

\[
D_{\pm1}(2\pm00) = -\frac{3}{\sqrt{15}} \frac{Q'p}{R_0^4} + 4\Delta \frac{4\pi}{\sqrt{5}} \frac{Q'p}{R_0^5} [Y_{10}(\overline{w}_1) - Y_{10}(\overline{w}_2)]
\]

\[
D_{\pm1}(002\pm) = \frac{3}{\sqrt{15}} \frac{Q'p}{R_0^4} - 4\Delta \frac{4\pi}{\sqrt{5}} \frac{Q'p}{R_0^5} [Y_{10}(\overline{w}_1) - Y_{10}(\overline{w}_2)]
\]

The first terms in equations (3.68) give rise to $\Delta J=0,2$ transitions as in the case of solid $H_2$. The smaller second
terms which are the ones of interest here can give rise to \( \Delta J=1 \) transitions in solid HD. If equations (3.68) are substituted in Eq. (3.66), then that part of the dipole moment denoted by \( \mu_v \), which will account for the \( \Delta J=1 \) transitions can be expressed as

\[
\mu_v(\overrightarrow{\alpha_1}, \overrightarrow{\alpha_2}; R_0) = 4\pi \sum_{\lambda_1 \mu_1, \lambda_2 \mu_2} A_{\lambda_1 \mu_1}(\overrightarrow{\alpha_1}) Y_{\lambda_1 \mu_1}(\overrightarrow{\alpha_1}) A_{\lambda_2 \mu_2}(\overrightarrow{\alpha_2}) Y_{\lambda_2 \mu_2}(\overrightarrow{\alpha_2})
\]

(3.69)

where the nonvanishing coefficients are given by

\[
A_{0}(1000) = -\xi e^{\frac{-R_0}{\sqrt{3}}} \frac{\Delta}{\rho} - \Delta \frac{12}{\sqrt{3}} \frac{Q'_p}{R_o^3} C(211;00)C(211;00)
\]

\[
A_{0}(0010) = \xi e^{\frac{-R_0}{\sqrt{3}}} \frac{\Delta}{\rho} - \Delta \frac{12}{\sqrt{3}} \frac{Q'_p}{R_o^3} C(211;00)C(211;00)
\]

\[
A_{0}(2010) = \Delta \frac{12}{\sqrt{15}} \frac{Q'_p}{R_o^3}
\]

\[
A_{0}(1020) = \Delta \frac{12}{\sqrt{15}} \frac{Q'_p}{R_o^3}
\]

(3.70)

\[
A_{\pm 1}(1\pm 10) = 4 \Delta \frac{Q'_p}{R_o^3} C(211;\pm1,0)C(211;00)
\]

\[
A_{\pm 1}(001\pm 1) = 4 \Delta \frac{Q'_p}{R_o^3} C(211;0,\pm1)C(211;00)
\]

\[
A_{\pm 1}(2\pm 10) = -\Delta \frac{4}{\sqrt{15}} \frac{Q'_p}{R_o^3}
\]

\[
A_{\pm 1}(102\pm 1) = -\Delta \frac{4}{\sqrt{15}} \frac{Q'_p}{R_o^3}
\]

Here pairs of spherical harmonics for the same argument have been expressed in terms of a single spherical harmonic and only those terms which can give rise to \( \Delta J=1 \) transitions have been kept. We now use the dipole moment (3.69) with coefficients (3.70) to calculate the intensities of \( \Delta J=1 \)
transitions in solid HD. The dipole moment corresponding to a molecule at $\vec{R}_i$ making a vibration-rotation transition is given by

$$\vec{\mu}_i = \sum_j \vec{\mu}(\vec{w}_i, \vec{w}_j; \vec{R}_{ij})$$  \hspace{1cm} (3.71)$$

where the sum runs over all molecules $j=i$ and where the pair moment for $i=1, j=2$ is given by Eq.(3.69). The matrix elements of the moment (3.61) corresponding to single transition are given by

$$\langle 00 | \vec{\mu}_{ij} | 1m, \vec{R}_i \rangle = \sum_{\mu \sigma_{ij}, l} (-1)^{l} \sum_j A_{\mu}^{j} (1\mu 00; R_{ij};) D_{ij}^{l*}(\hat{a}_{ij}) D_{ij}^{l*}(\hat{a}_{ij})$$ \hspace{1cm} (3.72)

where $\hat{a}_{ij}$ in the argument of the rotation matrices denotes the rotation that takes the hexagonal axis into the direction of the vector $\vec{R}_{ij} - \vec{R}_j \hat{a}_{ij}$ which connects molecules at $\vec{R}_i$ and $\vec{R}_j$. The wavefunctions of the crystal $|00\rangle$ and $|1m, \vec{R}_i\rangle$ are given by

$$|00\rangle = \prod_{j=1}^{N} Y_{00} (\vec{w}_j)$$ \hspace{1cm} (3.73)$$

and

$$|1m, \vec{R}_i\rangle = Y_{00} (\vec{w}_1) \ldots \sum_{\tilde{p}} D_{ij}^{l*}(\hat{a}_{ij}) Y_{1\tilde{p}} (\vec{w}_i) \ldots Y_{00}(\vec{w}_N)$$ \hspace{1cm} (3.74)$$

Eq.(3.73) represents the wavefunction of the ground rotational state of the crystal while Eq.(3.74) represents the wavefunction of the crystal for which a molecule at $\vec{R}_i$ is in the rotational state $J=1, m$ and the others are in the state $J=0$ and where $\vec{w}_i$ denotes the orientation of the molecule $i$ relative to $\vec{R}_i$ as polar axis. With the help of the Clebsch-Gordan Series (26)
and the relations
\[ \sum_n C(112; n, -n) C(11L; n, -n) = \delta_{jL} \]  
and
\[ D_{m\sigma}^L (\phi, \theta, \beta) = \frac{4\pi}{2L+1} (-1)^m Y_{l_m} (\theta, \phi). \]

Eq. (3.72) becomes
\[ \langle 00 | \mu_{x'v} | l m, \vec{R}_{iz} \rangle = \sum_{\mu L} \sum_j (-1)^{\mu L} \sqrt{\frac{4\pi}{2L+1}} C(11L; -v, -m) C(11L; -\mu, \mu) A_{\mu} (1\mu 00; \vec{R}_{iz}) Y_{l_m} (\theta_{ij}, \phi_{ij}) \]  
\[ \langle 00 | \mu_{x'v} | l m, \vec{R}_{iz} \rangle = \sum_{\mu L} \sum_j (-1)^{\mu L} \sqrt{\frac{4\pi}{2L+1}} C(11L; -v, -m) C(11L; -\mu, \mu) A_{\mu} (1\mu 00; \vec{R}_{iz}) Y_{l_m} (\theta_{ij}, \phi_{ij}) \delta_{v, -m} \]  
\[ \langle 00 | \mu_{x'v} | l m, \vec{R}_{iz} \rangle = \sum_{\mu L} \sum_j (-1)^{\mu L} \sqrt{\frac{4\pi}{2L+1}} C(11L; -v, -m) C(11L; -\mu, \mu) A_{\mu} (1\mu 00; \vec{R}_{iz}) Y_{l_m} (\theta_{ij}, \phi_{ij}) \delta_{v, -m} \]  
Summing over nearest neighbors, where \( \vec{R}_o \) is now the lattice constant, we have
\[ \langle 00 | \mu_{x'v} | l v, \vec{R}_{iz} \rangle = 12C(110; -v, v) \sum_{\mu L} (-1)^{\mu L} C(110; -\mu, \mu) A_{\mu} (1\mu 00; \vec{R}_o) \]  
\[ 12C(110; -v, v) \left\{ \sum_{\mu L} (-1)^{\mu L} \right\} C(110; 00) \left[ -\xi \frac{\alpha}{\beta} \frac{1}{\sqrt{3}} - \frac{12}{\sqrt{3}} \frac{Q\phi}{R_o^2} C(211; 00) C(211; 00) \right] \]  
\[ -C(110; -1, 1) \left[ 4\Delta \frac{Q\phi}{R_o^2} C(211; 10) C(211; 00) \right] \]  
\[ -C(110; 1, -1) \left[ 4\Delta \frac{Q\phi'}{R_o^2} C(211; -10) C(211; 00) \right] \]  
\[ -C(110; 1, -1) \left[ 4\Delta \frac{Q\phi'}{R_o^2} C(211; -10) C(211; 00) \right] \]
The Clebsch-Gordan coefficients have the following values

\[
\begin{align*}
C(110;0,0) &= \frac{-\sqrt{3}}{3} \\
C(110;-1,1) &= C(110;1,-1) = \frac{\sqrt{5}}{3} \\
C(211;0,0) &= -\frac{\sqrt{2}}{\sqrt{5}} \\
C(211;1,0) &= C(211;-1,0) = \frac{\sqrt{5}}{\sqrt{10}}
\end{align*}
\]

The quadrupolar terms sum to zero and only the overlap contribution remains. Then

\[
\left< 00 \left| \mu_{l,V} \right| 1, V, R_{x}\right> = -\frac{i\xi}{\sqrt{3}} C(110;-V,V) C(110;0,0) \xi e^{-\frac{8\pi^2}{\mathcal{P}}}
\]

The integrated absorption coefficient in units of cm\(^{-1}\) is given as (35)

\[
\bar{\alpha}[R_f(0)] = \frac{N}{V} \frac{2\pi^3}{3hC} \left| \mu_{\text{ot}} \right|^2
\]

where \(N/V\) is the number of molecules per unit volume and \(k_f = \frac{\hbar}{8\pi^2 \mathcal{M} \nu_0}\), \(M\) being the reduced mass and \(\nu_0\) the vibrational frequency of the molecule. Finally we obtain

\[
\bar{\alpha}[R_{1\leftarrow 0}(0)] = \frac{N}{V} \frac{2\pi^3}{3hC} \frac{16(\Delta)}{\mathcal{P}} \xi^2 e^{-\frac{2R_0}{\mathcal{P}}} \quad (3.80)
\]

Using \(H_2\) values for the overlap parameters;
\(\xi = 4.46 \times 10^{-9}\) e.s.u., \(\rho = 0.369\) Å (36), the value of Eq.(3.80) in solid HD will be

\[
\bar{\alpha}[R_{1\leftarrow 0}(0)] = 2.78 \times 10^{-3}\text{ cm}^{-1}
\]
(ii) The double transition \( Q_{1-0}(0) + R_0(0) \)

If the molecule \( j \) performs the rotational transition \( \Delta J = 1 \), then the matrix elements will be given by

\[
\langle 00 | \mu | 1m, R_j \rangle = \sum \langle -1 \rangle^\mu A_{\mu}(001\mu; R_{ij}) D_{\nu \mu}^*(\hat{\mu}_{ij}) D_{m-\mu}^*(\hat{\mu}_{ij})
\]

Assume isotropic absorption and make use of the theorem of spectroscopic stability (9) which states that the total intensity may be calculated with the help of unperturbed wavefunctions, i.e. with localized rotational excitations.

The contribution to the total intensity of the pair of molecules at \( R_i \) and \( R_j \) is proportional to

\[
\sum_i \left| \langle 00 | \mu | 1m, R_i \rangle \right|^2 = \sum \left| A_{\mu}(001\mu; R_{ij}) \right|^2
\]

Then the integrated absorption coefficient is

\[
\alpha \left[ Q_{1-0}(0) + R_0(0) \right] = \frac{N}{V} \frac{\kappa_i}{3hC} \sum_i \left| A_{\mu}(001\mu; R_i) \right|^2
\]

where the sum over \( i \) runs over all molecules except the central one, and \( R_i \) is the distance from the central molecule. The non-vanishing coefficients are

\[
A_0(0010) = \xi e^{\frac{Q_0}{3} \frac{1}{\rho}} - \Delta \frac{l^2}{R_0^2} \frac{Q_0}{R_0^2} C(211;00)C(211;00)
\]

\[
A_1(0011) = 4\Delta C(211;01)C(211;00) \frac{Q_0}{R_0^2}
\]

\[
A_{-1}(001-1) = 4\Delta \frac{Q_0}{R_0^2} C(211;0-1)C(211;00)
\]

and the Clebsch-Gordan coefficients have the following
values

\[ C(211;00) = -\sqrt{\frac{2}{5}} \]
\[ C(211;01) = C(211;01) = \frac{\sqrt{15}}{10} \]

Substituting equations (3.82) into Eq. (3.81) and summing over nearest neighbors, the result is

\[
\bar{\sigma} \left[ Q_{\perp 0} + R_0(0) \right] = \frac{N}{\sqrt{\hbar}} \frac{4\pi^3}{\kappa \hbar c} \frac{2}{12} \left( \frac{32}{25} \Delta^2 \frac{Q p'^2}{R_0^2} \right) + \frac{1}{3} \left( \frac{\Delta}{\kappa} \right) \left( \frac{R_0}{\kappa} \right) \left( \frac{Q p'}{R_0^2} \right)^2 \]

Using Hg values for \( Q = 0.45 \) \( \text{a}_e^2 \), and \( p' = 4.0 \) \( \text{a}_o^2 \), the value of \( \bar{\sigma} \) is

\[
\bar{\sigma} \left[ Q_{\perp 0} + R_0(0) \right] = 4.51 \times 10^{-4} \text{ cm}^{-1}
\]

(iii) The \( S_{\perp 0} + R_0(0) \) transition

The matrix elements for molecule \( i \) performing the transition \( \Delta J = 2 \) and \( j \) the transition \( \Delta J = 1 \), will be given by

\[
\left< 00 | \mu_i \nu_i | 2n, \vec{R}_i; 1m, \vec{R}_j \right> = \sum_{\mu_i \mu_2} (-1)^{\mu_1 + \mu_2} A_{\mu_i \mu_2} (2 \mu_1, 1 \mu_2; R_{ij}) D_{\mu_1 \mu_2}^{\ast} (\hat{a}_{ij}) D_{\mu_1 \mu_2}^{\ast} (\hat{a}_{ij}) D_{\mu_2 \mu_2}^{\ast} (\hat{a}_{ij})
\]

(3.83)

The integration absorption coefficient is then

\[
\bar{\sigma} \left[ S_{\perp 0} + R_0(0) \right] = \frac{N}{\sqrt{\hbar}} \frac{4\pi^3}{3 \hbar c} \sum_{\mu_i \mu_2} \sum_{L} \left| A_{\mu_i} (2 \mu_1, 1 \mu_2; \vec{R}_L) \right|^2
\]

The nonvanishing coefficients are
\[ A_0(2010) = \frac{12}{\sqrt{15}} \frac{\Delta}{R_0^2} Q' \phi \]
\[ A_1(2110) = A_{-1}(2-110) = -\frac{4}{\sqrt{15}} \frac{\Delta}{R_0^2} Q' \phi \]

Summing over nearest neighbors, we have

\[ \bar{\alpha} [S_{1 \leftarrow 0}(0)+R_0(0)] = \frac{N}{V} \frac{k}{\hbar} \frac{2 \pi^3}{3} 576 \left( \frac{\Delta}{R_0} \right)^2 \frac{Q'^2 \beta^2}{R_0^3} \]

Using \( Q' = 0.54 \text{ ea}_0 \), we obtain

\[ \bar{\alpha} [S_{1 \leftarrow 0}(0)+R_0(0)] = 1.06 \times 10^{-3} \text{ cm}^{-1} \]

For a hydrogen impurity in the HD host lattice, a factor of 1/2 should be put into Eq.(3.7) to take account of the HD-H\(_2\) pair. This will reduce the intensity by a factor of 1/4. There is a further reduction in the intensity of about 10% due to an increase in the lattice constant due to the presence of the H\(_2\) molecule.

### III.6 Phonon-Roton Coupling

In solid HD the coupling of the phonons with the J=1 rotons results from the displacement, \( \Delta = 0.123 \text{ Å} \), of the charge center from the mass center in the heteronuclear HD molecule. Therefore, the intermolecular potential, \( v(R'_{ij}) \), where \( R'_{ij} \) the distance between the charge centers of the molecules i and j, is not isotropic with respect to \( R_{ij} \), the vector joining the two centers of mass. Following the
treatment of Zaidi (21), we first expand $v(R'_{ij})$ to first order in $\Delta$ as

$$v(R'_{ij}) = v(R_{ij}) + g(R_{ij})Y_{10}(\hat{\omega}_{ij})$$

$$g(R_{ij}) = \left(\frac{4\pi}{3}\right)^{1/2} \Delta\nu'(R_{ij})$$

where $\hat{\omega}_{ij}$ denotes the orientation of the $i$-th molecule (central molecule) in the $R_{ij}$ frame (with polar axis along $R_{ij}$). The factor $g(R_{ij})$ couples the rotation of the central molecule to the positions of the perturbing molecules. Next we expand the potential

$$V = g(R_{ij})Y_{10}(\hat{\omega}_{ij})$$

between a pair of molecules $i,j$ in powers of the displacements, $\vec{u}_i$ and $\vec{u}_j$, of the molecules from their equilibrium positions. Putting $\vec{R}_{ij} = \vec{R}_{ij}^0 + \vec{S}$, where $\vec{S} = \vec{u}_i - \vec{u}_j$ denotes the relative displacement of the pair, and neglecting quadratic and higher order terms in this expansion, we find

$$V = g(R_{ij}^0)Y_{10}(\hat{\omega}_{ij}^0) + \sum_m g_m(R_{ij}^0)Y_{1m}(\hat{\omega}_{ij}^0)S_m^i (3.84)$$

where $\hat{\omega}_{ij}^0$ denotes the orientation of the central molecule in the $\vec{R}_{ij}^0$ frame, and $S_m^i$ denotes the spherical components of $\vec{S}$ with respect to $\vec{R}_{ij}^0$ as polar axis

$$S_0^i = S_z^i$$

$$S_2^i = \frac{1}{\sqrt{2}} (S_x^i + i S_y^i)$$
It is shown in Appendix B that $g_{m}(R_{ij})$ are given by

$$g_{0}(R_{ij}) = \langle \infty | g'(R_{ij}) | \infty \rangle$$

$$g_{\pm 1}(R_{ij}) = -\langle \infty | g(R_{ij}) / R_{ij} | \infty \rangle$$

where $| \infty \rangle$ denotes the ground state of HD crystal at 0°K.

According to the transformation law of spherical harmonics,

$$Y_{lm}(\omega_{ij}) = \sum_{n} D_{nm}^{l}(\tilde{R}_{ij}^{0}) Y_{ln}(\tilde{\omega}_{ij}) \quad (3.85)$$

where $\tilde{\omega}_{i}$ denotes the orientation of the $i$-th molecule relative to the hexagonal axis as polar axis and the coefficient $D_{nm}^{l}(\tilde{R}_{ij}^{0})$ is the rotation matrix for a rotation which carries the frame of reference whose polar axis is the hexagonal axis into the frame of reference whose polar axis is $\tilde{R}_{ij}^{0}$. Since $\tilde{S}$ is a vector, $S_{m}^{l}$ transforms under rotation like a spherical harmonic of order $l$,

$$S_{m}^{l} = \sum_{m'} D_{m'm}^{l}(\tilde{R}_{ij}^{0}) S_{m'} \quad (3.86)$$

in which $S_{m'}$ denotes the spherical components of $\tilde{S}$ with respect to the hexagonal axis as polar axis. Substituting Eq.(3.85) and Eq.(3.86) into Eq.(3.84), we find,

$$V = g(\tilde{R}_{ij}^{0}) \sum_{n} D_{n0}^{l}(\tilde{R}_{ij}^{0}) Y_{ln}(\tilde{\omega}_{i}) + \sum_{mn} B_{mn}(\tilde{R}_{ij}^{0}) Y_{ln}(\tilde{\omega}_{i}) S_{m} \quad (3.87)$$

where $B_{mn}(\tilde{R}_{ij}^{0}) = \sum_{m'} g_{m'}(\tilde{R}_{ij}^{0}) D_{m'm}^{l}(\tilde{R}_{ij}^{0}) D_{n-m'}^{l}(\tilde{R}_{ij}^{0}) \quad (3.88)$

With the help of the Clebsch-Gordan series (26), the product
of two rotation matrices becomes

$$D^I_{m'm'}(\vec{R}^o_{ij})D^I_{n'n}(\vec{R}^o_{ij}) = \sum_{L} C(1lL;m,n)C(1lL;m',-m')D^L_{m+n,d}(\vec{R}^o_{ij})$$

(3.89)

Eq. (3.88) reduces to

$$B_{mn}(\vec{R}^o_{ij}) = \sum_{L} \frac{4\pi}{2L+1} C(1lL;m,n) f_{L}(\vec{R}^o_{ij}) Y_{L,m+n}(\vec{R}^o_{ij})$$

(3.90)

in which $\vec{R}^o_{ij}$ denotes the polar angles of $\vec{R}^o_{ij}$ relative to the hexagonal axis and

$$f_{L}(\vec{R}^o_{ij}) = \sum_{m'} C(1lL;m,-m') g_{m'}(\vec{R}^o_{ij})$$

(3.91)

The total linear phonon-roton coupling, $H$, is obtained by summing the second term in Eq. (3.87) over all the neighbors of the central molecule,

$$H = \sum_{i} \sum_{m} B_{mn}(\vec{R}^o_{ij}) Y_{L,m,n}(\vec{R}^o_{ij}) S_{im}$$

(3.92)

where the $S_{im}$ are the spherical components of $\vec{S} = \vec{u}_i - \vec{u}_j$ with hexagonal axis as polar axis.

Next we express Eq. (3.92) in terms of the lattice vibrational coordinates. The displacement $u_i = \left(\vec{u}_i\right)$ of the molecule at the lattice site $\vec{R}^o_i$ can be expanded in the normal lattice vibrational modes as

$$\vec{u}_i = \left(\frac{\hbar}{2MN\omega_\lambda}\right)^{1/2} \sum_{k, \vec{R}^o_i} (a_\lambda + a_{-\lambda}^+) e^{i\vec{k}\cdot\vec{R}^o_i} \hat{e}_\lambda(\vec{k})$$

(3.93)

where $M$ is the mass of the molecule and $a_\lambda$ and $a_{-\lambda}^+$ are the phonon annihilation and creation operators,
The polarization vectors \( \hat{e}_p(\vec{k}) \) satisfy the orthonormality and the completeness relations

\[
\hat{e}_p(\vec{k}) \cdot \hat{e}_{p'}(\vec{k}) = \delta_{pp'}
\]

\[
(3.94)
\]

\[
\sum_p e_p(\vec{k}) e^*_p(\vec{k}) = \mathbf{1}
\]

From Eq.(3.93) we have

\[
\overline{S}_{im} = \overline{u}_i - \overline{u}_i = \left( \frac{\hbar}{2M \omega} \right)^{1/2} \sum_{k,\lambda} (a_{\lambda} + a_{\lambda}^+) \hat{e}_\lambda(\vec{k}) \cdot \hat{e}_\mu(\vec{k}) e^{i \vec{k} \cdot \vec{R}_{ij}} \left[ e^{i \vec{k} \cdot \vec{R}_{ij}} - 1 \right]
\]

\[
(3.95)
\]

Substituting Eq.(3.95) into Eq.(3.92), we obtain the following expression for the one phonon interaction

\[
H = \sum_{n,\lambda} A_{\lambda}(\vec{k}) (2N \omega) \frac{1}{2} g^{a}_{\lambda n}(\vec{k}) \sum_i e^{i \vec{k} \cdot \vec{R}_{ij}} Y_{1n}(\omega_i)
\]

\[
(3.96)
\]

\[
g^{a}_{\lambda n}(\vec{k}) = \left( \frac{\hbar}{2M} \right)^{1/2} \sum_{L,\mu} \left( \frac{4 \pi}{2L+1} \right) C(1lL; m, n) \hat{e}_\lambda(\vec{k}) \cdot \hat{e}_\mu(\vec{k}) Y_{Lm+n}(\vec{k})
\]

\[
(3.97)
\]

\[
I_{L, m+n} = \sum_{i, j} f_L(R_{ij}^0) Y_{L, m+n}(\vec{R}_{ij}^0) \left[ \exp(i \vec{k} \cdot \vec{R}_{ij}^0) - 1 \right]
\]

\[
(3.98)
\]

\[
f_L(R_{ij}^0) = \sum_{m'} C(1L; m', -m') g_{m'}(R_{ij}^0)
\]

\[
(3.99)
\]

where \( A_{\lambda}(\vec{k}) = a_{\lambda}(\vec{k}) + a_{\lambda}^*(-\vec{k}) \)

From Eq.(3.99) it follows that only \( L=0 \) and 2 give nonvanishing \( f_L(R_{ij}^0) \). In solid HD, \( f_L(R_{ij}^0) \) falls off rather
rapidly for large $R$ so that the sum over $j$ in Eq.(3.98) is restricted to the 12 nearest neighbors of the central molecule. In the continuum approximation, this sum will be replaced by an integral over a sphere

$$\sum_{j} \rightarrow \frac{12}{4\pi} \int d\Omega$$

(3.100)

With these approximations we obtain for the nonzero $I_{0,0}(\vec{k})$ as

$$I_{0,0}(\vec{k}) = \frac{12}{4\pi} f_0(a)(4\pi)^{\frac{-1}{2}} \int [\exp(\vec{k} \cdot \vec{R}_{ij}) - 1] d\Omega$$

$$= 12(4\pi)^{\frac{3}{2}} f_0(a) \left[ \int_0^\pi \exp(ik\cos\theta) d(\cos\theta) - 1 \right]$$

(3.101)

and the $I_{2,m+n}(\vec{k})$ as

$$I_{2,m+n}(\vec{k}) = 12 f_L(a) \int Y^*_{2,m+n}(\hat{R}_{ij}) \left[ \exp(\vec{k} \cdot \vec{R}_{ij}) - 1 \right] d\Omega$$

By expanding $\exp(\vec{k} \cdot \vec{R}_{ij})$ in spherical harmonics

$$\exp(\vec{k} \cdot \vec{R}_{ij}) = 4\pi \sum_{L=0}^{\infty} i^L j_L(kR_{ij}) \sum_{\nu} Y_L^\nu(\hat{R}_{ij}) Y_{L\nu}^*(\vec{k})$$

and using the orthogonality property of spherical harmonics

$$(4\pi)^{-\frac{1}{2}} \sum_{\nu} Y^*_{2,m+n}(\hat{R}_{ij}) Y_{L\nu}(\hat{R}_{ij}) d\Omega = \delta_{L,2} \delta_{m+n,\nu}$$

we obtain

$$I_{2,m+n}(\vec{k}) = -12 j_2(ka) f_2(a) Y^*_{2,m+n}(\vec{k})$$

where $a$ is the lattice constant, and $j_2$ is the spherical Bessel function. It follows that the $\vec{k}$ dependence of $g_{\lambda n}(\vec{k})$
should be appreciable over the whole Brillouin zone. As $k \to 0$, $g_{\lambda n}(\vec{k}) \to 0$, as expected physically.

Using the intermolecular potential, $v(R)$ for solid $H_2$ (40) and with damping constant $\beta = 1 \text{ cm}^{-1}$, Zaidi (21) estimates for solid HD that $|g_{\lambda n}|^2/\beta \sim 10^4 \text{ cm}^{-2} \sim (\omega - \epsilon_s)^2$. This estimate shows a strong phonon-roton coupling.

III.7 Expression for the One-Phonon Branch in terms of the Lattice Vibrational Spectrum

The intensity of the phonon branch which arises due to the creation of a single phonon depends on the matrix element of the induced dipole moment and the number of energy states available to the phonon in the final state. Since the density of these states is essentially determined by the lattice vibrational spectrum, it is possible to express the intensity of the phonon branch in terms of the lattice vibrational mode. Although the treatment is quite general and can be applied to any rotational or vibrational transition in the spectrum, for the sake of illustration we will consider the $U_0(0)$ line.

The $U_0(0)$ transition arises from the induced dipole moment due to electric field of the hexadecapole moment of the HD molecule in the solid. The total induced dipole moment by the hexadecapole moment of the molecule at the origin of coordinates is from Eq.(3.54)
\[
\mu_v = \sum_i \mu_{v_i} \\
= 4\pi \left( \frac{5}{11} \right)^2 \frac{PQ_4}{a^6} C(4,1,5; m, v, m+v) Y_{4,m}^*(\hat{\Omega}_0) \sum_i \left( \frac{a}{R_i} \right)^6 Y_{5,m+v}(\hat{\Omega}_i)
\]

(3.102)

where \( \hat{\Omega}_0 \) represents the orientation of molecule 0 at the origin with respect to the hexagonal axis and \( \hat{\Omega}_i \) stands for the angular coordinates of the i-th molecule with respect to the hexagonal axis in the h.c.p. lattice.

To take account of the lattice vibration, we replace \( \mid R_i \rangle \) in Eq.(3.102) by \( \mid R_i - \bar{u}_i \rangle \) where \( \bar{u}_i = \bar{u}_0 - \bar{u}_1 \), \( \bar{u}_1 \) and \( \bar{u}_0 \) being the vibrational displacements of the molecules i and 0 from their equilibrium lattice sites. Following Lien (37), we expand \( \mid R_i - \bar{u}_i \rangle \) in a power series in \( u_{i0} / R_i \) and keep only the linear term, the total induced dipole moment becomes

\[
\mu_v = \sum_m F(m, v, \hat{\Omega}_0) \sum_i \left( \frac{a}{R_i} \right)^6 Y_{5,m+v}(\hat{\Omega}_i) \left[ 1 + 6 \left( \frac{\bar{u}_i}{R_i} \right) \right] 
\]

(3.103)

where \( F(m, v, \hat{\Omega}_0) \) is given by

\[
F(m, v, \hat{\Omega}_0) = 4\pi \left( \frac{5}{11} \right)^2 \frac{PQ_4}{a^6} C(4,1,5; m, v, m+v) Y_{4,m}^*(\hat{\Omega}_0)
\]

The integrated absorption coefficient per HD molecule per unit volume is defined as

\[
\alpha = \frac{1}{N} \int \alpha(\varepsilon) \, d\varepsilon = \frac{8\pi^3}{3\hbar} \sum_{m', m''} \frac{1}{2J'' + 1} \left| \frac{\mu_{m'm''}}{2J'' + 1} \right|^2
\]

(3.104)

where \( \mu_{m'm''} = \langle J''M'' \mid \langle \text{vac} \mid \mu_v \mid J'M' \rangle \mid \bar{K} \rangle \) is the transition matrix element of \( \mu_v \) between the initial state \( \mid J''=0, M''=0 \rangle \mid \text{vac} \rangle \) i.e. a product of rotational state \( Y_{0,0}(\hat{\Omega}_0) \)
and the vacuum phonon state, and the final state 
\( |J'=4, M'\rangle \), i.e. a product of the rotational state
\( Y_{4, m} (\Omega_0) \) and the one phonon state with wavevector \( \vec{k} \). Since
the lattice is assumed to be at absolute zero there is no
contribution due to the absorption of phonons.

The first term in Eq.(3.103) represents the zero
phonon transition. The second term which is linear in \( \vec{u}_{i\alpha} \) is
responsible for a single phonon creation and by substituting
the second term into Eq.(3.104), we obtain

\[
|\mu_{u}^{M'M''}\rangle = \langle 0, 0 | \langle \text{vac} | \mu_{i\nu} | 4, M'\rangle_{1\vec{k}} \langle 0, 0 | \langle \text{vac} | \mu_{i\nu} | 4, M'\rangle_{1\vec{k}}^* \rangle_{0, 0}
\]

(3.105)

To evaluate the matrix element in Eq.(3.105), it is
convenient to expand the displacements in terms of the
emission and absorption operators

\[
\hat{u}_{i\alpha} = \left( \frac{\hbar}{2N M} \right) \sum_{\lambda} \left( \frac{1}{\omega_{\lambda}} \right) (a_{\lambda} + a_{\lambda}^+) \hat{\epsilon}_{\lambda}(\vec{k})(1 - e^{i\vec{k}\cdot\vec{R}_{i}})
\]

(3.106)

where the phonon creation and annihilation operators and the
polarization vectors \( \hat{\epsilon}_{\lambda}(\vec{k}) \) are defined as in Eq.(3.93) and
Eq.(3.94). By substituting Eq.(3.106) into Eq.(3.105) and
evaluating the matrix element we get the following
expression

\[
|\mu_{u}^{M'M''}\rangle = \sum_{m,v} F^2(m, v, \Omega_0) \sum_{i,j} \sum_{\lambda, p} \omega^{-1}_{\lambda,p}[a_{\lambda}^{\dagger} [R_{i}\cdot R_{j}]_{R_p}]^{7} Y_{5, m+v}(\Omega_0) Y_{5, m+v}(\Omega_0)^{*} \hat{\epsilon}_{\lambda}(\vec{k}) \cdot \hat{\epsilon}_{\lambda}(\vec{k}) \cdot \hat{\epsilon}_{\lambda}(\vec{k}) (1 - e^{i\vec{k}\cdot\vec{R}_{i}})(1 - e^{i\vec{k}\cdot\vec{R}_{i}})
\]

(3.107)

where \( F^2(m, v, \Omega_0) = (6/a)^{3}(\frac{\hbar}{2MN}) \left| \langle J'' M'' | F(m, v, \Omega_0) | J'M'\rangle \right|^2 \)
Eq. (3.107) can be reduced to

$$\left| \mu_0 \left. M'' M'' \right| \right|^2 = \sum_{m} \sum_{v} F_{m,v}^{r} (m,v,\hat{\Omega}) \sum_{i,j} \left( \frac{a^2}{R_i R_j} \right)^2 Y_{5,m+v}(\hat{\Omega}_i) Y_{5,m+v}(\hat{\Omega}_j)$$

$$\sum_{\hat{R}_i,\hat{R}_j} \omega_{\hat{R}_i,\hat{R}_j} G_{ij}(\hat{\Omega}) \left( \hat{e}_p(\hat{R}_i) \cdot \hat{R}_j \right) \left( \hat{e}_p(\hat{R}_i) \cdot \hat{R}_j \right)$$

(3.108)

where $G_{ij}(\hat{\Omega}) = 1 - e^{i \vec{k} \cdot \vec{R}_i} - e^{i \vec{k} \cdot \vec{R}_j} + e^{i \vec{k} \cdot (\vec{R}_i - \vec{R}_j)}$

To evaluate Eq. (3.108), we make some simplifying assumptions which can be justified on the basis of the lattice dynamics of the h.c.p. lattice. First, we assume that the frequencies $\omega_{\hat{R}_i,\hat{R}_j}$ are independent of the direction of the wave vector. Secondly, we assume that the polarization vectors are real and that the vector $\hat{e}_3(\hat{\Omega})$ corresponding to the longitudinal mode is along the wave vector

$$\hat{e}_3(\hat{\Omega}) = \hat{\Omega} = \frac{\vec{k}}{|\vec{k}|}$$

(3.109)

In this approximation the completeness relation can be expressed as follows,

$$\sum_{p=1}^{l} \hat{e}_p(\hat{\Omega}) \hat{e}_p^*(\hat{\Omega}) = \mathbb{I} - \hat{k} \hat{k}$$

(3.110)

With the aid of the relations (3.109) and (3.110) Eq. (3.108) can be expressed as follows,

$$\left| \mu_0 \left. M'' M'' \right| \right|^2 = \sum_{m} \sum_{v} F_{m,v}^{r} (m,v,\hat{\Omega}) S(m+v,\vec{R}_i,\vec{R}_j) \{ A_i + A_i \}$$

(3.111)

where $S(m+v,\vec{R}_i,\vec{R}_j)$ is given by

$$S(m+v,\vec{R}_i,\vec{R}_j) = \sum_{i,j} \left( \frac{a^2}{R_i R_j} \right)^2 Y_{5,m+v}(\hat{\Omega}_i) Y_{5,m+v}(\hat{\Omega}_j)$$
and $A_l(\omega)$ and $A_t(\omega)$ are defined as follows

$$A_l(\omega) = \sum_{k} \left\{ \omega_{k l}^{-1} \right\} \left\{ \begin{pmatrix} \frac{k \cdot \vec{R}_i}{R_i} \\ \frac{k \cdot \vec{R}_j}{R_j} \end{pmatrix} \right\}$$  \hspace{1cm} (3.112)$$

$$A_t(\omega) = \sum_{k} \left\{ \omega_{k l}^{-1} \right\} \left\{ \begin{pmatrix} 1 - \frac{k \cdot \vec{R}_i}{R_i} \\ \frac{k \cdot \vec{R}_j}{R_j} \end{pmatrix} \right\}$$  \hspace{1cm} (3.113)$$

We replace the first Brillouin zone by a sphere and average the equations (3.112) and (3.113) over all directions of the wave vector. These averages are performed by using the following expressions, derived in Appendix C

$$\langle (\vec{x} \cdot \vec{R}_j) (\vec{x} \cdot \vec{R}_j) \rangle = \frac{k^2}{3} (\vec{R}_i \cdot \vec{R}_j)$$  \hspace{1cm} (3.114)$$

$$\langle (\vec{x} \cdot \vec{R}_j) (\vec{x} \cdot \vec{R}_j) e^{ik \cdot (\vec{R}_i - \vec{R}_j)} \rangle = \frac{k^2}{3} (\vec{R}_i \cdot \vec{R}_j) \left\{ J_0(kR_{ij}) + J_2(kR_{ij}) \right\}$$  \hspace{1cm} (3.115)$$

$$\langle (\vec{x} \cdot \vec{R}_j) (\vec{x} \cdot \vec{R}_j) e^{ik \cdot (\vec{R}_i - \vec{R}_j)} \rangle = \frac{2k^2}{3} (\vec{R}_i \cdot \vec{R}_j) \left\{ J_0(kR_{ij}) - 2J_2(kR_{ij}) \right\}$$  \hspace{1cm} (3.116)$$

where the brackets indicate average over a sphere of radius $k$, and the $J_n(x)$ is the spherical Bessel function of order $n$. By substituting Eq. (3.114) through Eq. (3.116) into Eq. (3.112) and Eq. (3.113) and rearranging, we get the following expressions for the longitudinal and transverse branches,

$$A_l(\omega) = \sum_{k} \left\{ \omega_{k l}^{-1} \right\} \left\{ \frac{\vec{R}_i \cdot \vec{R}_j}{3R_iR_j} - \frac{2}{3} \frac{\vec{R}_i \cdot \vec{R}_j}{R_iR_j} \left[ J_0(kR_{ij}) - 2J_2(kR_{ij}) \right] \right\}$$  \hspace{1cm} (3.117)$$

$$A_t(\omega) = \sum_{k} \left\{ \omega_{k l}^{-1} \right\} \left\{ 1 - \frac{2}{3} \frac{J_0(kR_{ij}) + J_2(kR_{ij})}{R_iR_j} + \frac{R_{ij}^2}{4R_iR_j} J_2(kR_{ij}) \right\}$$
After substituting Eq. (3.117) and Eq. (3.118) into Eq. (3.111), we have

\[
\left| \mu_{\nu}^{\text{M}^{\text{M}}^{\text{M}}} \right|^2 = \sum_{m} \mathcal{P}^2(m, \nu, \hat{\Omega}_0) \sum_{i,j} \left( \frac{a^2}{R_i R_j} \right)^7 Y_{5, m+\nu}(\hat{\Omega}_i)^* Y_{5, m+\nu}(\hat{\Omega}_j) \left\{ A_i(\omega) + A_j(\omega) \right\}
\]

(3.119)

Because of the short range nature of the induced moment, the summations over \( i \) and \( j \) can be restricted to the nearest neighbors of the central molecule, i.e., \( R_i = R_j = a \) where \( a \) is the lattice constant of HD in an h.c.p. lattice.

Furthermore, the terms for which \( R_{ij} > a \) make only a small contribution to the total induced moments, and may be neglected. Thus restricting the summation over \( i \) and \( j \) to all pairs of neighbors for which \( R_{ij} = a \), we obtain the following expression for the matrix element,

\[
\left| \mu_{\nu}^{\text{M}^{\text{M}}^{\text{M}}} \right|^2 = \sum_{m} \mathcal{P}^2(m, \nu, \hat{\Omega}_0) \sum_{i,j} Y_{5, m+\nu}(\hat{\Omega}_i)^* Y_{5, m+\nu}(\hat{\Omega}_j) \left\{ \omega^{-1} \right\} 8 - 16 J_0(ka) + 32 J_2(ka) + \frac{1}{3} J_0(kR_{ij}) + \frac{1}{3} J_2(kR_{ij}) \]

(3.120)
Finally, Eq.(3.121) can be written as

\[
\left| \begin{array}{c}
\hat{\mu}_\nu^M
\end{array} \right|^2 \sum_{m', \nu'} F_{m, \nu}^2(m', \nu, \hat{\Omega}_0) \sum_{i,j} Y_{5, m+\nu}(\hat{\Omega}_i) Y_{5, m+\nu}^*(\hat{\Omega}_j) \sum_k \left\{ \omega_{kl}^{-1} 2 \right\} [\hat{\alpha}_l F_l(ka) + \omega_{k1}^{-1} F_\ell(ka)]
\]

(3.122)

where

\[
F_{m, \nu}^2(m', \nu, \hat{\Omega}_0) = 24 \pi \left( \frac{\hbar}{12 \pi M^N} \right)^2 \frac{\rho Q_4}{a^2} C(4, 1, 5; m, \nu, m+\nu) Y_{4 m}(\hat{\Omega}_0) | J''M'' >
\]

and \( F_\ell(ka) \) and \( F_l(ka) \) are given by

\[
F_\ell(ka) = 6 - 14 J_0(ka) + 37 J_2(ka)
\]

\[
F_l(ka) = 6 - 2 J_0(ka) - 37 J_2(ka)
\]

After applying a symmetry argument appropriate to an h.c.p. lattice, Eq.(3.122) is nonvanishing only when \( m+\nu = \pm 3 \). We define the lattice sum \( S' \) as

\[
S' = \sum_{i,j} Y_{5, 3}(\hat{\Omega}_i) Y_{5, 3}^*(\hat{\Omega}_j) = \left[ \sum_i Y_{5, 3}(\hat{\Omega}_i) \right]
\]

\[
= \left[ \frac{1}{32 \sqrt{\frac{770}{2\pi}}} \right]^2 S^2
\]

where the lattice sum \( S \) has the following value after summing over the nearest neighbor molecules,
From Section III.4 (ii) and Eq. (3.122) we obtain the nonvanishing matrix elements of the induced moment as follows:

\[
|\mu_0^{0,3}|^2 = |\mu_{0,-3}|^2 = B^2 S^2 P(ka) \frac{4}{45\pi}
\]

\[
|\mu_1^{0,2}|^2 = |\mu_{1,-2}|^2 = B^2 S^2 P(ka) \frac{7}{45\pi}
\]

\[
|\mu_1^{0,-4}|^2 = |\mu_{1,4}|^2 = B^2 S^2 P(ka) \frac{1}{180\pi}
\]

where \( B = 24\pi \left( \frac{2\pi}{22M} \right)^{\frac{1}{2}} \frac{pQ_4}{a^2} \left( \frac{385}{1024\pi} \right)^{\frac{1}{2}} \)

\( Q_4 = \langle 0,0 | Q_4 | u,4 \rangle \) is the ro-vibrational matrix element of the hexadecapole moment of the HD molecule.

and \( F(ka) = \sum_k \left[ \omega_k^{-1} F_\ell(ka) + \omega_k^{-1} F_\ell(ka) \right] \)

From Eq. (3.104), we have

\[
\int \alpha(f) df = \frac{8\pi^3 N}{3h} \sum_{M'M''\nu} \left| \mu_{M'M''}^{\nu} \right|^2
\]

(3.125)

where \( \alpha(f) \) is the absorption coefficient per wavelength of the crystal, \( f \) is the frequency in sec\(^{-1}\) and \( N \) is the number of molecules in the ground state.

Substituting Eq. (3.124) into Eq. (3.125), we have

\[
\int \alpha(\omega) d\omega = \frac{4\pi^2}{3h} B^2 S^2 \left\{ \omega_{\ell k}^{-1} F_\ell(ka) + \omega_{\ell k}^{-1} F_\ell(ka) \right\}
\]

(3.126)

To express Eq. (3.126) in terms of the lattice vibrational
spectrum we assume the following dispersion relation between the frequency and the wave vector.

\[ \omega_{kp} = \frac{2Km c_p}{\pi} \sin \frac{\pi k}{2Km} \]  

(3.127)

where \( K_m \) is the radius of the sphere equivalent to the first Brillouin zone, and \( C_p \) (\( p=1,2,3 \)) is the velocity of long wave \( p \)-th mode. \( C_p \) is obtained by averaging the expression \( \frac{\omega_{kp}}{|k|} \) over all directions of \( k \) in the neighborhood of the origin. For long wave \( k \gg 0 \), Eq.(3.127) becomes

\[ \omega_{kp} = \frac{2Km c_p}{\pi} \frac{\pi k}{2Km} = C_p k \]

This reduces to the familiar isotropic Debye model. With the help of Eq.(3.127), we transform \( F_k (ka) \) and \( F_t (ka) \) to the frequency space and by replacing the summation \( k \) by an integration over \( \omega_k \), we get the following expression for the absorption profile of the one-phonon branch of the \( U_q(0) \) transition

\[
\int a(\omega) d\omega = \frac{2\pi}{3h} B^2 S^2 \int \frac{1}{\omega} \left[ 6-14J_0(\omega_l) + 37J_2(\omega_t) \right] g_t(\omega) d\omega
+ \int \frac{1}{\omega} \left[ 6-2J_0(\omega_t) - 37J_2(\omega_t) \right] g_t(\omega) d\omega
\]

or

\[
a(\omega) = \frac{2\pi}{3h} B^2 S^2 \left| \frac{1}{\omega} \left[ 6-14J_0(\omega_l) + 37J_2(\omega_t) \right] g_t(\omega) \right|
+ \left[ 6-2J_0(\omega_t) - 37J_2(\omega_t) \right] g_t(\omega) \right| \]

(3.128)

where \( g_t(\omega) \) and \( g_t(\omega) \) are the normalized phonon density spectrum for the longitudinal and transverse modes respectively. The frequencies \( \omega_t \) and \( \omega_t \) are given by
where the subscript $p$ denotes the longitudinal or transverse mode and $c$ is the speed of light.

Since the total phonon branch belonging to a particular transition can be divided into separate branches corresponding to the creation of one, two or more phonons, to first approximation, we can write the total absorption coefficient as a sum of phonon branches in the form

$$a(\omega) = \sum_n a_n(\omega)$$

In general, there are six branches of the vibrational spectrum (three optical branches and three acoustical branches) in an h.c.p. lattice. The approximation we made in leading to Eq.(3.110) implies that there are only three branches of the vibrational spectrum. This approximation is not too serious, since the optical branches can be regarded as the continuations of the corresponding acoustical branches.

Due to the overlap of the branches arising from the higher order phonon processes, a comparison of the intensities arising from different order phonon processes is hard to realize experimentally.
The experimental apparatus described in Chapter II was used to study the infrared absorption spectrum of solid HD in the entire region 500-5000 cm$^{-1}$. The measurements reported here are the first ones made on solid HD using a Fourier transform spectrometer at a resolution of 0.04 cm$^{-1}$. All previous infrared experiments on solid HD made use of grating instruments. In view of the high resolution of a Fourier transform spectrometer, the present experimental data are regarded as the most accurate to date.

The HD gas used in the experiments was prepared by the action of D$_2$O on LiAlH$_4$ as described by Fookson et al. (17). The gas contained approximately 7% of normal H$_2$; this became evident when spectral features were found which correspond to combinations of HD and H$_2$ frequencies. The HD molecule is heteronuclear and hence the distinction between symmetric and antisymmetric rotation levels, which is important in H$_2$ and D$_2$, does not exist. There is no para or ortho modifications of HD. At a temperature of 160K because of the
smallness of the Boltzmann factor compared with the energy difference between the J=0 and J=1 rotational states, nearly all of the molecules are in the J=0 rotational state. One would then expect the spectrum of solid HD to resemble that of para-H₂ or ortho-D₂. Although there is overall similarity between para-H₂ and HD spectra, there are striking differences in detail which give special interest to the HD spectrum.

IV.1 The U₁₋₀(0) Band

Most of the features of the HD spectrum can be identified on the basis of the frequency alone. By using the gas phase vibrational and rotational constants of HD quoted from Herzberg and Huber (38) assuming the molecular constants are not perturbed in the solid, we calculate 883.26 cm⁻¹ for the U₀(0) transition and 4469.82 cm⁻¹ for U₁₋₀(0) transition of HD. The U symbolizes a transition with ΔJ=4, the zero subscript refers to the vibrational state v=0 (pure rotational transition) or v=1 (first excited vibrational state), and the number inside the bracket indicates the initial rotational state of HD. Thus U₁₋₀(0) indicates a transition from the state characterized by vibrational quantum number v=0 and rotational quantum number J=0 to v=1, J=4 state. Similarly U₀(0) indicates a transition from the state characterized by v=0, J=0 to the state with v=0, J=4.
The observed wavenumbers are 885.18 cm\(^{-1}\) for \(U_0(0)\), and 4472.23 cm\(^{-1}\) for \(U_{1\rightarrow 0}(0)\) of HD. All these observed frequencies are in good agreement with those calculated from the gas phase constants. Thus the identification of these lines is made solely on the basis of wavenumber and the small amount of shift in line position between the experimental result and the gas phase prediction indicates that the effect of intermolecular forces on the rotational motion of HD molecules is small. The \(U_0(0)\) feature is a relatively sharp transition with a FWHM (full width at half maximum) of 2.2 cm\(^{-1}\), characteristic of a single transition. The calculated integrated absorption coefficient using the parameters of \(H_2\) that are unknown for HD is \(1.5 \times 10^{-15}\) cm\(^3\)/sec. in good agreement with the experimental value of \(1.2 \times 10^{-15}\) cm\(^3\)/sec. The \(U_{1\rightarrow 0}(0)\) feature has a FWHM of 4.8 cm\(^{-1}\) and the experimentally determined integrated absorption coefficient of \(1.7 \times 10^{-16}\) cm\(^3\)/sec.

Both \(U_0(0)\) and \(U_{1\rightarrow 0}(0)\) transitions are accompanied by the weak and broad phonon branches with the peaks located at 41.1 cm\(^{-1}\) and 38 cm\(^{-1}\) from their respective zero-phonon U transitions. In order to show features hidden inside the high frequency noise, we smoothed out the high frequencies by using a digital filtering algorithm with a 1.25 cm\(^{-1}\) data averaging interval. The smoothed phonon branch profile of \(U_0(0)\) transition is shown in Fig.22. This graph has a lot of features hidden inside it. We will refer to this when we
come to the discussion of phonon branch in Chapter V. In order to display the structure of the absorption profile more clearly, the spectrum of the $U_0(0)$ and $U_1(0)$ together with their phonon branches are shown on an expanded scale in figures 10, 11 and 12.

IV.2 The $V_{1-0}(0)$ Band

The $V_0(0)$ transition arises from the 32-polar induced dipole moment of the HD molecule. Based on the gas phase data, we calculate the transition frequencies to be 1313.48 cm$^{-1}$ for $V_0(0)$ transition and 4885.01 cm$^{-1}$ for the $V_{1-0}(0)$ transition. Here the $V$ symbolizes a transition with $J=5$. The observed frequencies are 1318.26 cm$^{-1}$ and 4886.66 cm$^{-1}$ for the $V_0(0)$ and $V_{1-0}(0)$ transitions respectively. Both $V_0(0)$ and $V_{1-0}(0)$ are weak transitions and we are unable to locate the peaks of their phonon branches. The calculated integrated absorption coefficient for $V_0(0)$ line using values of $H$ for any parameters that are unknown for HD is $1.29 \times 10^{-16}$ cm$^3$/sec in good agreement with the experimental value of $1.1 \times 10^{-16}$ cm$^3$/sec. The absorption profiles for the $V_0(0)$ and $V_{1-0}(0)$ transitions are shown on an expanded scale in Figures 13 and 14. The experimentally obtained frequencies, integrated absorption coefficients of the various components of the U and V transitions of solid HD, along with their calculated values are listed in Table IV.1.
Figure 10. $U_0(0)$ transition of solid HD (7% $n$-$H_2$ impurity).
Figure 11. $U_0(0)$ and $U_0^R(0)$ transition of solid HD (7% $n$-$H_2$ impurity).
Figure 12. $U_{1+0}^T(0)$ and $U_{1+0}^R(0)$ transitions of solid HD (7% n-H$_2$ impurity).
Figure 13. $V_0(0)$ transition of solid HD. (7% n-H$_2$ impurity)
Figure 14. $V_{1-0}(0)$ transition of solid HD (7% n-$\text{H}_2$ impurity). Sharp lines overlapping the broad $V_{1-0}(0)$ feature are due to $\text{H}_2\text{O}$ present in the optical path.
TABLE 1.

Wavenumbers and integrated absorption coefficients of various components of the U and V bands of solid HD; 16°K, zero pressure.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Wavenumber (CM⁻¹)</th>
<th>FWHM (CM⁻¹)</th>
<th>Integrated absorption coefficient(CM³/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
<td>Calculated</td>
<td>Experimental</td>
</tr>
<tr>
<td>U₀(0)</td>
<td>885.18</td>
<td>883.26</td>
<td>2.2</td>
</tr>
<tr>
<td>U₀⁺(0)</td>
<td>925.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>U₁⁺₀(0)</td>
<td>4472.3</td>
<td>4469.82</td>
<td>4.8</td>
</tr>
<tr>
<td>U₁⁻₀(0)</td>
<td>4509.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V₀(0)</td>
<td>1318.26</td>
<td>1317.48</td>
<td></td>
</tr>
<tr>
<td>V₁⁻₀(0)</td>
<td>4886.66</td>
<td>4885.01</td>
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</tr>
</tbody>
</table>
IV.3 The $S_{1-0}(0)+S_{0}(0)$, $Q_{1-0}(0)+T_{0}(0)$ and $T_{1-0}(0)$ Band

The $S_{1-0}(0)+S_{0}(0)$ absorption feature, shown in Fig.15, arises when a vibration-rotation transition, $\Delta v=1$, $\Delta J=2$ in one molecule is accompanied by a rotation transition, $\Delta v=0$, $\Delta J=2$, in another. This band is a broad feature with a total extent of about 40 cm$^{-1}$ and is centered on the calculated frequency for this transition. The $S_{1-0}(0)+S_{0}(0)$ band in solid HD displays an interesting structure in which three components, at 4138.24, 4147.5 and 4159.85 cm$^{-1}$ are observed. The first two components are broad but the third component is a relatively narrow and symmetrical line with a FWHM of approximately 4 cm$^{-1}$ and stands out with a peak absorption about twice that of the rest of the band. This component is assigned a double transition $Q_{1-0}(0)+T_{0}(0)$ in which one molecule making a vibrational transition, $\Delta v=1$, $\Delta J=0$ is accompanied by a rotational transition, $\Delta v=0$, $\Delta J=3$, in another and is centered on the calculated frequency for this transition. The first broad component at 4138.24 cm$^{-1}$ is identified as a single $T_{1-0}(0)$ transition since it is centered on the calculated frequency for this transition.

The central component at 4147.5 cm$^{-1}$ is due to the H$_2$ impurity present in the crystal since it appears close to the frequency of the $Q_{1-0}(1)$ transition in solid H$_2$ and this sharp feature is identified as the $Q_{1-0}(1)$H$_2$ line. Consequently the broad central component is a feature of the
Figure 15. Fundamental absorption spectrum of HD in the region 4130 to 4230 cm$^{-1}$.
structure of the $S_{1-0}(0)+S_0(0)$ band due to HD only. The same absorption feature was observed but misinterpreted by Crane and Gush (16) who attributed the whole band as the $S_{1-0}(0)+S_0(0)$ double transition alone. The dip in the profile at 532.36 cm$^{-1}$ indicates the possibility of a pure rotational $T_0(0)$ transition. But, unfortunately, it is found to be overlapped by the double transitions $2S_0(0)$ of HD. The experimentally obtained frequencies of the various components of the $S_{1-0}(0)+S_0(0)$, $Q_{1-0}(0)+T_0(0)$ and $T_{1-0}(0)$ band along with their calculated values are listed in Table IV.2.

IV.4 The HD-$H_2$ Combination Transitions

The HD-$H_2$ combination transitions $Q_{1-0}(0)H+D_0(1)H$, $Q_{1-0}(1)H+S_0(0)HD$ and $S_{1-0}(0)HD+S_0(1)H_2$ are shown in Fig.16. These features are present as a result of a small amount of $H_2$ impurity in the HD crystal. As the notation indicates, these are double transitions where an HD molecule together with an $H_2$ molecule simultaneously takes part in the vibration-rotation transition $AV=1$, $AJ=2$. Only the transitions involving ortho $H$ were observed, because with a 7% normal $H_2$ impurity, the para-$H_2$ content ($<1\%$) is too small to have any observable effect.

Since the $H_2$ molecules in the crystal are effectively isolated from each other, a rotational excitation in a $H_2$
<table>
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<th>Transition</th>
<th>Wavenumber (cm⁻¹)</th>
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</thead>
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<td>Experimental</td>
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<tr>
<td>$T_{1-0}(0)$</td>
<td>4138.24</td>
</tr>
<tr>
<td>$S_{1-0}(0) + S_{0}(0)$</td>
<td>4147.5</td>
</tr>
<tr>
<td>$Q_{1-0}(0) + T_{0}(0)$</td>
<td>4159.85</td>
</tr>
<tr>
<td>$Q_{1-0}(1)H_2$</td>
<td>4146.6</td>
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</table>
Figure 16. Fundamental absorption spectrum of solid HD in the region 4380 to 4540 cm\(^{-1}\).
TABLE 3.

Wavenumbers of the components observed in the HD-H₂ combination transitions in solid HD (7% H₂ impurity), 16K, zero pressure

<table>
<thead>
<tr>
<th>Transition</th>
<th>Wavenumber (CM⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
</tr>
<tr>
<td>Q₁₋₀ (0) HD + S₀ (1) H₂</td>
<td>4211.49</td>
</tr>
<tr>
<td>S₀ (0) HD + Q₁₋₀ (1) H₂</td>
<td>4416.5</td>
</tr>
<tr>
<td>S₁₋₀ (0) HD + S₀ (1) H₂</td>
<td>4473.0</td>
</tr>
</tbody>
</table>
molecule will be localized on that molecule. Consequently, the transitions \( Q_{1 \rightarrow 0}(0) \) HD + S\(_{0}(1)\) H\(_{2}\) and \( S_{1 \rightarrow 0}(0) \) HD + S\(_{0}(1)\) H\(_{2}\) will be sharp features as is the case observed. The full widths at half maximum for the two double transitions were measured as 1 and 3 cm\(^{-1}\) respectively. The former has a width characteristic of a vibrational exciton band but the width of the latter is about 7 cm\(^{-1}\). The observed and calculated frequencies of these combination transitions are given in Table IV.3.

**IV.5 The \( Q_{1 \rightarrow 0}(0) \) Transition**

The \( Q_{1 \rightarrow 0}(0) \) line in pure solid HD is forbidden because the induced dipole moments vanish when summed over the lattice. The appearance of the \( Q_{1 \rightarrow 0}(0) \) line in the spectrum is attributed to the presence of ortho-H\(_{2}\) impurities, which is the reason given for the appearance of the same line in para-H\(_{2}\) crystals (39). It is assumed that the \( Q_{1 \rightarrow 0}(0) \) line arises as a result of a simultaneous transition in which a \( \Delta V=1, \Delta J=0 \) transition in the host HD crystal is accompanied by an orientational transition in an ortho-H\(_{2}\) molecule. As mentioned in the Introduction, this is due to anisotropic intermolecular interaction between the J=0 HD molecule and the J=1 H\(_{2}\) molecule. The overall width of the line is about 3 cm\(^{-1}\) which is characteristic of a vibrational exciton band. The FWHM is about 0.6 cm\(^{-1}\). The frequency of the \( Q_{1 \rightarrow 0}(0) \) line is 3624.8 cm\(^{-1}\) which is 7.35 cm\(^{-1}\) lower than
Figure 17. $Q_{1+0}(0)$ transition of solid HD
its value in the gas phase. This indicates that the vibrational frequency is perturbed by the intermolecular forces active in the crystal. In order to display the structure of the absorption profile more clearly, the spectrum of the $Q_{1-0}(0)$ transition is shown on an expanded scale in Fig.17. The satellite structure surrounding the main peak is due to the electric quadrupole-quadrupole (EQQ) interaction between a pair of ortho-hydrogen molecules. The location of the peak position and the intensity of each component can be calculated using the same method as given in Ref. (40).

The broad band marked $Q^R$ in Fig.18 is the phonon branch accompanying the $Q_{1-0}(0)$ transition. The frequency shift of the maximum of this phonon branch from the frequency of the zero-phonon is 65 cm$^{-1}$. The intensity of the $Q^R$ branch drops abruptly near 3690 cm$^{-1}$ and the profile in this frequency region resembles closely the high frequency end of Debye phonon spectrum with its characteristic sharp cutoff. This resemblance should be regarded as largely accidental, because in H$_2$ and D$_2$ the intensity of the phonon branch falls relatively slowly and the profile extends to much higher frequencies than the Debye limit. Crane and Gush (16) attribute to the fact that in solid HD the phonon branch has effectively been split into two parts by a vanishing of the matrix elements of the dipole moment near 3706 cm$^{-1}$. This results from a coupling
between the lattice vibrations and the rotational motion of the HD molecule, the frequency of which falls within the continuum of phonon state. In Fig. 18 we show the $Q_{1-0}(0)$ phonon branch together with the zero-phonon transition.

IV.6 The $R_{1-0}(0)$ Transition

We were unable to observe the $R_{1-0}(0)$ transition, because at a path length of 26 mm the absorption was essentially 100%. In Fig. 19 we show an experimental spectrum of the $R_{1-0}(0)$ transition and its accompanying phonon branch obtained by Crane and Gush (16). The sharp $R_{1-0}(0)$ line at 3709.70 cm$^{-1}$ is assumed to result from the single molecule transition with $\Delta v=1, \Delta J=1$ because firstly it appears close to the calculated frequency for this transition, and secondly the intensity is approximately that expected for a single transition. This transition is strictly forbidden in the case of $H_2$ and $D_2$ but is allowed in HD because HD is not homonuclear. In the HD molecule the center of mass and the center of charge do not coincide. As a result, the rotational motion and translational motion in the lattice are coupled, the frequency of which falls within the continuum of phonon states. It is believed that in solid HD the phonon branch has been split into two parts, labelled as $Q^R$ and $Q^R'$ in Fig. 19. It was concluded by Crane and Gush that the gap in the phonon spectrum at 3706 cm$^{-1}$ is due to the incapability of the HD molecule to excite modes of
Figure 19. Fundamental absorption spectrum of solid HD at 1.9 K, 1.00 cm path, recorded with a spectral resolution of 0.3 cm^{-1}. (Ref. 16)
vibration of its frequency of rotation.
CHAPTER V

DISCUSSION AND CONCLUSIONS

The experiments reported in this thesis are the first ones made on solid HD using a Fourier transform spectrometer at a resolution of 0.04 cm\(^{-1}\). The multiplex advantage of such a spectrometer has permitted us to record good-quality spectra in the entire spectral region 500--5000 cm\(^{-1}\) within a matter of a few hours. In view of its high resolution the present experimental data are regarded as the most accurate to date. In this Chapter we will give a general discussion of the experimental results and the interpretation of these results based on the theoretical treatment presented in Chapter III. In section V.1, we will give a comparison between our theoretical predictions of the integrated intensity and the experimental values assuming our experimental data are accurate. In that section, we will also give a general comparison between our interpretation of the absorption mechanism and that developed by Van Kranendonk. In section V.2, we will give a general discussion on the phonon branch with particular attention paid to the one-phonon density of states as revealed from
the absorption profile. In section V.3, the importance of
the present research in solid hydrogens is discussed in
terms of nuclear fusion as well as cosmo logical point of
view. Finally, the thesis is concluded in section V.4.

V.1 The Zero Phonon Transition

We have used two different methods to calculate our
theoretical predictions of the integrated intensity for
various transitions in our solid HD experiments: (i)
Multipole field induced dipole moment method and (ii) Van
Kranendonk's "exponential-4" model. In this section we will
give a comparison between these two methods based on the
accuracy in the calculated integrated intensities assuming
our experimental data are accurate. First we made use of
Gray's (14) derived formula for the induced moment between
two non-overlapping charges to calculate the integrated
intensities for the $V_0(0)$, $U_0(0)$ and $T_0(0)$ transitions
assuming a rigid h.c.p. lattice. As shown in Table IV.1, our
theoretical predictions of the integrated absorption agree
with the experimental results very well. This close
agreement shows that our interpretation of the absorption
mechanism is essentially correct. Earlier, Poll and Tipping
(11) using Van Kranendonk's theory calculated the integrated
intensity of the $U_{1-0}(0)$ line of solid parahydrogen. It
incorporates a "reduction factor" $\xi(=0.8)$ as a means of
allowing for the nonrigidity of the real lattice, but leads to an intensity that is smaller than the higher resolution measurement (12) by almost a factor of 0.6. The accuracy of our method over those of Poll and Tipping is apparent as far as higher order transitions are concerned. Further, our method has distinct advantage in that the infrared activity of individual sublevels are automatically included in the derivation. This information is useful if one wants to study the absorption with polarized light in a single crystal. However, one drawback in our method is that the absorption mechanism is non-operative for the \( Q(\Delta J=0) \) and \( R(\Delta J=1) \) transitions when the overlap induction effect becomes dominant. Here we give a comparison between our predicted intensity for the \( S_0(0) \) transition obtained from section III.4 and that calculated by Van Kranendonk (9). The discrepancy between the theoretical and the known (41) experimental intensities is 25% by our method while it is 9.5% by Van Kranendonk's model. This shows that the approximate region of validity for our method is from \( \Delta J=2 \) and higher while Van Kranendonk's model is applicable to all transitions.

In section III.5, we calculated the intensity of the \( R_{1-0}(0) \) transition using Van Kranendonk's model which resulted in an intensity roughly twice the experimental value as measured by Crane and Gush (15). Comparison between the theoretical prediction and our experimental result is
difficult because with our 26 mm cell, the absorption for the $R_{1-0}(0)$ transition is essentially 100%.

If our experimental data are assumed to be accurate, then the small discrepancy between the theoretical and the experimental intensities must come from the theoretical part.

One possible reason is for HD the appropriate matrix elements of hexadecapole moment, quadrupole moment and polarizability are not available at present and we have to assume the corresponding values for H$_2$ in our calculations.

The second reason is that in the real solid, the molecules probably do not rotate exactly about their centers of mass as we have assumed here but about some point intermediate between it and the center of charge. In the absence of a dynamical theory of the HD crystal we assume that the molecules in the solid rotate about their centers of mass, these lying on the lattice sites of a rigid h.c.p. crystal structure.

The third reason comes from the approximation involved in simplifying the coordinates transformation from the center of charge to the center of mass system as is done in section III.4. We neglect the coordinate transformation of spherical harmonics and keep terms only up to first order in $\Delta$, the displacement between the charge center and the mass center.
The fourth reason is due to the zero-point motion of the HD molecules. At zero pressure in solid HD, the widths of the (non-Gaussian) single-particle distribution function is about \((10 \sim 15)\%\) of the nearest neighbor distance \((1)\). The zero-point motion not only has profound effects on the interaction constants, causing them to be renormalized, but also seriously modifies the solid dipole moment and polarizability, directly affecting the observed spectral functions. The phonon renormalization consists in the replacement of the intermolecular interactions for the rigid lattice by the expectation values of these interactions over the zero-point lattice vibrations. Harris \((42)\), using a variational Hartree single-particle Gaussian type wave function modified by a short range Jastrow correlation factor, showed that the result of averaging the EQQ interaction is simply to renormalize the rigid lattice coupling parameter by a constant and found that the reduction factor \(\xi = 0.93\) for \(H_2\) and \(D_2\). Luryi and Van Kranendonk \((42)\), renormalized the multipole interaction by expanding the interaction potential between a \(2l_1\)- and a \(2l_1\)-pole molecular charge distribution in powers of relative displacement of two molecules from their equilibrium positions and averaging the potential over a pair distribution function. They found that the relative motion of the molecules has smaller amplitude in the direction of their separation than in the transverse direction and that all the multipole interactions are reduced by the zero-point
lattice motion. This will lead to some reduction factor in the lattice sum in our calculation. If we assume that this reduction factor is the main source of discrepancy, then we found that the reduction factor $\xi$ for HD should not be less than 0.88 from our data.

Considering the model used and the above mentioned factors involved, the agreement between our theoretical predictions of integrated intensity and the experimental results are as good as can be expected.

V.2 The Phonon Branch

The translational motion of the molecules in the solid has the form of lattice vibrations. In the case of induced infrared spectra, the lattice vibrations are infrared active by virtue of the strong dependence of the induced dipole moments responsible for the absorption on the intermolecular separations. In addition to the pure vibrational and rotational transitions which give rise to the sharp vibrational and rotational lines (zero-phonon branches), there are in the solid vibrational and transitions which are accompanied by the creation of one or more phonons. Such transitions give rise to the phonon branches belonging to the corresponding zero-phonon transitions. It is also possible that no vibrational or rotational transitions accompany the creation of phonons in the absorption process,
such transitions give rise to the pure phonon spectra extending from zero frequency up to roughly two or three times the maximum Debye frequency of the solid (15).

Phonon branches, which actually dominate the infrared absorption spectra of solid hydrogens where they account for a large fraction of the intensity, have been the main subject of discussion ever since their first discovery in the 1950's. Both the zero-phonon transition and the phonon branch are intimately related to the crystal structure and the intermolecular forces. Study of these absorptions in turn will give us information about the solid crystal structure, the intermolecular interaction and the lattice vibrations. However, the phonon density of states of solid hydrogens is hard to extract by any means. Neutron scattering is the only method to determine the phonon density states of solid hydrogens. There is a conjecture that the observed phonon branch absorption intensity is proportional to the one phonon density of states of solid hydrogen as are inferred by Balusubramanian et al. (13) and Kuo et al. (44). The intensity of the phonon branch exhibits a peak position and the profile in this frequency region resembles the one-phonon density of states obtained by neutron diffraction techniques on an h.c.p. crystal of solid hydrogen (45). This resemblance should be regarded as largely accidental. Although there is overall similarity between them, there are differences in detail.
There are two major discrepancies that distinguish the phonon branch absorption profile from the true one-phonon density of states. These are:

(i) The profile does not exhibit a square law fall-off at low frequencies.

(ii) The profile fails to exhibit a cut-off at high frequencies but rather a tail section extending beyond the characteristic Debye cut off frequency.

Further, a calculation of the phonon branch intensity based on nearest neighbor interactions (section III.7) shows that the phonon branch absorption profile and the one-phonon density of states are not simply related but rather a function involving the lattice vibrational spectrum is convolved with the phonon density spectrum.

The phonon branches can be considered as a combination tones of the fundamental ro-vibrational frequency of the molecule with the phonon frequency. The total phonon branch belonging to a particular zero-phonon transition can be divided into separate branches corresponding to the creation of one, two or more phonons. According to the calculation of Poll and Van Kranendonk (15) the integrated intensity of the n-phonon branch decreases rapidly with the order n. Further, since the distribution of an n-phonon spectrum extends over a frequency range of about n times that for a one-phonon branch, the absorption profile that is revealed in the one-phonon branch will be diffused out and the peak
absorption will be lower in the higher order branches. It is very difficult to separate a particular phonon branch from the rest of the branch because of the severe overlap of various phonon branches.

In Fig. 20 we show the one-phonon spectrum of the Debye model with Debye temperature $\theta_D = 120^\circ$K and in Fig. 21 we show the one-phonon density of states directly measured by using neutron scattering techniques on an h.c.p. crystal of solid $\text{H}_2$ (46). One immediately notes the resemblances between these two figures. That is, a square law fall-off at low frequencies and a sharp cut-off at high frequencies. Although the corresponding data are lacking for HD at present, we may assume the general features persist in the case of HD. The third peak shown in Fig. 21 has been verified by Mertens and Biem (47), who utilizing the time-dependent Hartree type wavefunction modified with a short range two-body correlation function, show a third peak located at 105 cm$^{-1}$ followed by a sharp cutoff. We may expect the one-phonon absorption profile to follow the same pattern. It is clear that the $U_0(0)$ phonon branch absorption profile of solid HD shown in Fig. 22 does not exhibit an absorption feature due to a single phonon but rather a multiple-phonon absorption profile with a characteristic tail section beyond the Debye cutoff frequency. This is a general phenomenon for the rotational transition where there is a significant contribution due to higher order phonon
Figure 20. One phonon density of states obtained by Debye model ($\theta_D = 120^\circ$K)
Figure 21. One phonon density of states from neutron diffraction (Ref. 46)
Figure 22. Smoothed phonon branch $u^R_0(0)$ of solid HD
processes and the one phonon absorption profile will be diffused out.

In Fig. 23 we show a phonon branch of the pure vibrational $Q_1^0(0)$ transition of solid parahydrogen. Since the phonon branch of the $Q_1^0(0)$ transition owes most of its intensity to the one phonon processes (15), we may assume that only one phonon is emitted as a result of the absorption of radiation. As a consequence of this the phonon branch shown in Fig. 23 is a true representation of one-phonon absorption and from which we can extract the one-phonon density of states if we know the lattice vibrational spectrum of the solid.

The phonon branches of infrared absorption are reflections of the spectrum of the normal modes of the crystal lattice vibrations. In Fig. 22, we show a smoothed phonon branch profile of the $U_0^0(0)$ transition of HD. In Fig. 24 we show an experimental spectrum of the $S^R$ branch of the pure rotational $S_0^0(0)$ transition of HD (48). Let us compare Fig. 22 with Fig. 24. In Fig. 22, we have a peak at 41 cm$^{-1}$ a bump with valleys on the sides at 48 cm$^{-1}$ and 62 cm$^{-1}$ and a prominent dip at 85.6 cm$^{-1}$. In Fig. 24 we find three kinks before the $S^R$ peak. These three kinks are located at 33 cm$^{-1}$, 49 cm$^{-1}$, and 60 cm$^{-1}$ away from the $S_0^0(0)$ line. The position of these kinks matches closely the positions of the peak and two sidelobes of the central bump of the $U^R$ branch of HD. In a harmonic solid the Debye frequency distribution
Figure 23. $Q_{1-0}(0)$ and $Q_{1-0}^R(0)$ of solid parahydrogen

<table>
<thead>
<tr>
<th>$n$</th>
<th>$\delta_{d}(Q_{1}(0))$ (sec$^{-1}$ cm$^2$)</th>
<th>$\delta_{d}(S_{1}(0))$ (sec$^{-1}$ cm$^2$)</th>
<th>$\delta_{d}(Q_{1}(0)+S_{1}(0))$ (sec$^{-1}$ cm$^2$)</th>
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<td>0.01</td>
<td>0.01</td>
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</table>
Figure 24. The absorption spectrum of pure rotational band of solid HD recorded with a resolution of 0.25 cm$^{-1}$ at $T=4.2^\circ K$ and $L=1$ cm. (Ref. 48)
for a three dimensional crystal has $3n$ branches, where $n$ is the number of molecules per unit cell; in the case of an h.c.p. lattice, this gives six branches. The number of observable branches within a phonon branch should be six. However, at most only three components or maxima for each phonon branch are observed in the present HD experiment as are observed by Treffler et al. (48). This interesting feature is unexplained at present. This may due to the degeneracy of the lattice vibrational modes in an h.c.p. lattice.

In Fig. 24, the phonon branch associated with the $S(0)$ feature consists of two parts, $S^R$ and $S^I_R$. The minimum between the two peaks is located at a frequency above $S(0)$ equal to the $R(\Delta J=1)$ transition frequency, i.e. $89 \text{ cm}^{-1}$. In Fig. 19 we show the $R_{1-0}(0)$ transition obtained by Crane and Gush (16). The $R_{1-0}(0)$ line occurs at a frequency $79 \text{ cm}^{-1}$ from the $Q_{1-0}(0)$ line. At first glance, the approximate coincidence of the $R_{1-0}(0)$ transition and the $Q_{1-0}(0)$ phonon dip position makes it appear that the effect is due to the existence of the allowed electric dipole moment. This possibility is ruled out by Souers et al. (49) who attribute the mechanism as associated with the anisotropic interaction which couples the $J = 1$ rotational states with the lattice vibrations as discussed by Zaidi (21). Because of the interaction of the rotational motion of the HD molecule with the lattice vibrations, the density of phonon states in the
neighborhood of the rotational $1\rightarrow 0$ transition frequency is strongly perturbed and shows a pronounced minimum as observed experimentally. Such interaction occurs only for heteronuclear diatomic molecules. By this mechanism the phonon spectrum itself is affected, and therefore a similar dip is found at about the same displacement from any zero-phonon transition of solid HD. The strength of the coupling between the rotational and the translational motions depends on the anisotropic interaction between the molecules. The HD molecule, being the largest anisotropic of the heteronuclear species, is expected to have the largest prominent phonon dip; this is evident in Fig.22 which shows a prominent dip at 85.6 cm$^{-1}$.

As a result of the coupling between the rotation of the HD molecule and the lattice vibration, it is possible for the lattice vibration to promote transitions from the $J=0$ to $J=1$ state. The frequency of the $J=0$ to $J=1$ transition in HD is 89 cm$^{-1}$ referenced to $Q_{1\rightarrow 0}(0)$ line whereas the Debye frequency is considerably lower, presumably about 73 cm$^{-1}$ (31) a value between those of $H_2$ and $D_2$. Excitation of the $J=1$ state can only result if modes exist in the crystal whose frequencies are above the Debye limit. That this is the case is evident in Fig.25.
Figure 25. Density of lattice vibrational modes for solid $H_2$.
(from Ref. 32)
V.3 Present Research in Solid Hydrogens

In this section we will give a brief discussion on the status and significance of the present research in solid hydrogens from the nuclear fusion and the cosmological point of view.

(i) In Nuclear Fusion

Frozen hydrogen-deuterium (H-D) may be used as a nuclear fuel in magnetic and inertial confinement fusion. The infrared absorption spectrum of HD becomes active if the radiation-activated fuel contains a small amount of tritium impurity. The radiation-induced infrared lines in solid hydrogens are first observed by Souers et al. (50) who attribute the radiation-induced lines as being due to the absorption by dipoles located on the molecules of the host species. These dipoles are induced by the electric field of neighboring ions. The ions are created by the beta particles emitted in the radioactive decay of the tritium impurity in the HD crystal. These radiation-induced infrared lines actually dominate the fusion process where they account for a large fraction of the intensity. The discovery of every single new transition and its accompanying phonon branch in solid HD not only has its research interest but also can account for the unexplained amount of energy loss in a nuclear fusion process.
(ii) In Cosmology

One of the most important unsolved problems in cosmology is the question, "Is the universe open or closed?". In the standard model of Big Bang, most of the matter in the universe is in the form of hydrogen and helium. Hydrogen comprises about 70-80% of all matter in the universe by weight, while helium comprises about 20-30% by weight. Hydrogen is believed to be the primordial element out of which all the heavier elements were synthesized. One needs high temperatures to produce heavier nuclei from hydrogen nuclei. Before the synthesis of helium in the early universe, protons and neutrons had to combine to make deuterium nuclei. The deuterium nucleus was then synthesized into helium through the intermediate steps of tritium and helium-three. It is rather difficult to synthesize deuterium in the center of very hot stars because of its instability, so most of the deuterium that occurs in the universe is believed to be primordial, that is, that which was synthesized in the first few minutes after the big bang. If the universe is closed, the present density of the universe is relatively large (greater than the critical density). If this is the case, the density of protons and neutrons in the phase of the universe in which nucleosynthesis occurred must have been correspondingly large. Thus a large density would have ensured that more of the deuterium that was formed would be converted into helium than would be the case for a
smaller density. Thus one would expect a smaller abundance of deuterium at present if the universe is closed than otherwise. In principle, therefore, we can decide if the universe is open or closed by measuring accurately the present abundance of deuterium and comparing it with a certain critical density. Therefore knowing the universe's present density enables us to draw conclusions about its present state and eventual future.

V.4 Conclusions

In summary, the important features of this thesis are the following:

(1) The U(ΔJ=4) and V(ΔJ=5) transitions in the pure rotational and vibration-rotation regions have been observed for the first time.

(2) An attempt to interpret these transitions by hexadecapolar and 32-polar induced dipole moment yields theoretical values of the integrated absorption coefficients which are in good agreement with the experimental data.

(3) The R(ΔJ=1) transitions in solid HD are unique features which arise from the mass asymmetry of an HD molecule.

(4) A dip located at 85.6 cm⁻¹ in the phonon branch of the U transition of HD has been observed. A similar dip in the phonon branch is found at about the same displacement from
any zero-phonon transition of HD. This mechanism is associated with the anisotropic interaction which couples the J=1 rotational states with the lattice vibrations as discussed by Zaidi (21).

(5) Phonon branches are reflections of the spectrum of the normal modes of the crystal-lattice vibrations. It is possible to express the intensity of the one-phonon branch in terms of the lattice vibrational spectrum.

(6) Under certain approximations, the phonon branch intensity is proportional to the phonon density of states, but the phonon branch absorption profile is not simply related to the one-phonon density of states.

(7) The comparison of the one-phonon density of states obtained by neutron scattering techniques and that of the Debye model shows that lattice vibrational modes in solid hydrogens exist beyond the Debye cutoff frequency.

(8) The absorption features that distinguish the HD spectrum from that of \( \text{H}_2 \) are due to HD molecules alone and are not a result of any impurities in the crystal.

(9) The measurements reported here are the first ones made on solid HD using a Fourier transform spectrometer. All previous infrared experiments on solid HD made use of a grating spectrometer.

(10) This is the first attempt to obtain the HD spectrum in
the 500 cm$^{-1}$ to 2000 cm$^{-1}$ region. All previous work concentrated on the fundamental band and its overtones. Only a few workers studied the pure rotational band.
APPENDICES

Appendix A. The Symmetry Elements of the H.C.P. Lattice and the Reduction of a Lattice Sum.

There are three symmetry elements in a h.c.p. lattice which applied about an arbitrary point 0 leave the h.c.p. lattice invariant:

(1) A 3-fold rotation axis of symmetry designated by $C_3$, where $C$ stands for cyclic and rotation through about the $Z$ (hexagonal) axis produces an orientation indistinguishable from the original.

(2) Reflection $\sigma_h$ about a horizontal mirror plane through 0 perpendicular to the $Z$ axis.

(3) Reflection $\sigma_v$ about three vertical mirror planes which contain the $Z$ axis and one of the nearest neighbors in the other horizontal plane. The effect of these operations on the angular coordinates $(\theta, \phi)$ are as follows:

$$C_3 \theta = \theta, \quad C_3 \phi = \phi \quad (A.1)$$

$$\sigma_h \theta = \pi - \theta, \quad \sigma_h \phi = \phi \quad (A.2)$$

$$\sigma_v \theta = \theta, \quad \sigma_v \phi = 2\phi - \phi \quad (A.3)$$
In Eq. A.3, $\phi_o$ represents the azimuth of the vertical mirror plane.

Now we have a lattice sum of the form

$$S = \sum_{i} \left( \frac{a}{R_i} \right)^2 Y_{6,m+\nu}(\hat{\mathbf{r}}_i)$$  \hspace{1cm} (A.4)

Application of $C_3$ to Eq. A.4 yields

$$C_3S = e^{2\pi i \frac{m+\nu}{3}} S = S$$

This implies $(m+\nu)/3 = n$, where $n$ is an integer. That is

$$m+\nu = 3n$$  \hspace{1cm} (A.5)

Because of the absolute value of $m+\nu$ must not be greater than 6 as restricted by the spherical harmonic $Y_{6,m+\nu}(\hat{\mathbf{r}}_i)$, $m+\nu$ can only have 0, ±3, and ±6.

Application of $\sigma_h$ to Eq. A.4 yields

$$S = (-1)^{6-(m+\nu)} S = S$$  \hspace{1cm} (A.6)

This implies that $6-(m+\nu)$ must be even. Thus $m+\nu$ must be even. From Eqs. A.4 and A.6 we see that the lattice sum vanishes except $m+\nu = 0$, 6 or -6.

Symmetry element $\sigma_h$ gives no further restriction.
Appendix B. Expansion of the anisotropic potential in powers of displacements.

We start with the anisotropic potential

\[ \mathcal{V} = g(R_{ij}) Y_{10}(\hat{\omega}_{ij}) \]  

(B.1)

and rotate the orientation of the molecule \( i \) according to the transformation law of spherical harmonics,

\[ Y_{10}(\hat{\omega}_{i\ell}) = \sum_{m} D_{m0}^{1}(R_{ij}) Y_{1m}(\hat{\omega}_{ij}) \]  

(B.2)

where \( D_{m0}^{1}(R_{ij}) \) is the rotation matrix for a rotation which carries the frame of reference whose polar axis is along \( \overrightarrow{R}_{ij} \) into the frame of reference whose polar axis is along \( \overrightarrow{R}_{ij} \).

From Eq. (B.1) and Eq. (B.2) we have

\[ \mathcal{V} = \sum_{m} h_{1m}(\overrightarrow{R}_{ij}) Y_{1m}(\hat{\omega}_{ij}) \]  

(B.3)

where

\[ h_{1m}(\overrightarrow{R}_{ij}) = \frac{2\pi}{\sqrt{3}} g(R_{ij}) Y_{1m}^{*}(\overrightarrow{R}_{ij}) \]  

(B.4)

Since \( \overrightarrow{R}_{ij} = \overrightarrow{R}_{ij}^{\circ} + S = \overrightarrow{R}_{ij}^{\circ} + \overrightarrow{u}_{j} - \overrightarrow{u}_{i} \), we expand Eq. (B.4) in powers of the displacement \( S \) and neglect quadratic and higher order terms, we find

\[ h_{1m}(\overrightarrow{R}_{ij}) = h_{1m}(\overrightarrow{R}_{ij}^{\circ} + S) \]

\[ = h_{1m}(\overrightarrow{R}_{ij}^{\circ}) + (-1)^{\mu} S_{\mu} \nabla_{\mu} h_{1m}(\overrightarrow{r}) \bigg|_{r=\overrightarrow{R}_{ij}^{\circ}} + \text{quadratic term} \]  

(B.5)

Since \( \nabla_{\mu} h_{10}(\overrightarrow{r}) \bigg|_{r=\overrightarrow{R}_{ij}^{\circ}} \) is zero unless \( \mu = 0 \), in this case,
\[ \nabla_0 h_{10}(\vec{r}) = \frac{4\pi}{3\sqrt{5}} C(1,1,2;0,0) Y_{20}(\vec{r}) \left( \frac{d}{d\vec{r}} - \frac{1}{r} g \right) \]
\[ - \frac{4\pi}{3} C(1,1,0;0,0) Y_{00}(\vec{r}) \left( \frac{d}{d\vec{r}} + \frac{2}{r} g \right) \]  
(B.6)

The last equation is obtained by using the gradient formula (3.31).

Now
\[ Y_{20}(\vec{r}) |_{00} = \sqrt{\frac{2}{4\pi}} \]
\[ Y_{00}(\vec{r}) |_{00} = \sqrt{\frac{1}{4\pi}} \]
(B.7)

and
\[ C(1,1,2;0,0) = \sqrt{\frac{2}{3}} \]
\[ C(1,1,0;0,0) = -\sqrt{\frac{1}{3}} \]  
(B.8)

we have from Equations (B.6) through (B.8), the following expression,
\[ \nabla_0 h_{1m}(\vec{r}) |_{\vec{r}=R_{ij}^o} = \frac{dg}{d\vec{r}} |_{\vec{r}=R_{ij}^o} = g'(R_{ij}^o) \]  
(B.9)

Similarly,
\[ \nabla h_{1,-1} = \nabla h_{11} \]
\[ = \frac{4\pi}{3\sqrt{5}} C(1,1,2;1,-1) Y_{20}(\vec{r}) (g' - \frac{1}{r} g) \]
\[ - \frac{4\pi}{3} C(1,1,0;1,-1) Y_{00}(\vec{r}) (g' + \frac{2}{r} g) \]  
(B.10)

and
\[ \nabla h_{1,-1} |_{\vec{r}=R_{ij}^o} = \nabla h_{11} |_{\vec{r}=R_{ij}^o} = - \frac{g(R_{ij}^o)}{R_{ij}} \]  
(B.11)

Comparing equations (B.5), (B.11) and (B.9) with Eq.(3.84)

we see that
\[ g_0(R_{ij}^o) = \langle 0,0 | g'(R_{ij}^o) | 0,0 \rangle \]
and

\[ g_{\pm 1}(R_{ij}) = - \langle 0,0 | \frac{g(R_{ij})}{R_{ij}} | 0,0 \rangle \]

where \( | 0,0 \rangle \) denotes the ground state of the HD crystal at \( 0^\circ \text{K} \).
Appendix C. Evaluation of Average

We consider the expression

\[ I(\vec{R}_i, \vec{R}_j) = \langle \vec{k} \cdot \vec{R}_i \vec{k} \cdot \vec{R}_j e^{i\vec{k} \cdot (\vec{R}_i - \vec{R}_j)} \rangle \]  \hspace{1cm} (C.1)

Where the brackets indicate an average over the surface of a sphere of radius \( R \). This average is performed by integrating over the solid angle, \( d\Omega_k = \sin\theta_k d\theta_k d\phi_k \) where \((k, \theta_k, \phi_k)\) are the polar coordinates of the vector \( \vec{k} \).

By introducing the variables \( \vec{r} \) and \( \vec{R} \), defined as

\[ \vec{r} = \vec{R}_i - \vec{R}_j \]
\[ \vec{R} = \vec{R}_i + \vec{R}_j \]

The expression (C.1) can be expressed as follows,

\[ I(\vec{R}_i, \vec{R}_j) = \langle \frac{1}{4} \{ [\vec{k} \cdot (\vec{R}_i + \vec{R}_j)]^2 - [\vec{k} \cdot (\vec{R}_i - \vec{R}_j)]^2 \} e^{i\vec{k} \cdot \vec{r}} \rangle \]
\[ = \langle \frac{1}{4} \{ (\vec{k} \cdot \vec{R})^2 e^{i\vec{k} \cdot \vec{r}} - (\vec{k} \cdot \vec{R})^2 e^{i\vec{k} \cdot \vec{r}} \} \rangle \]
\[ = \frac{1}{4} \left[ S(\vec{R}, \vec{r}) - S(\vec{r}, \vec{r}) \right] \]  \hspace{1cm} (C.2)

Where \( S \) is given by

\[ S(\vec{R}, \vec{r}) = \langle (\vec{k} \cdot \vec{R})^2 e^{i\vec{k} \cdot \vec{r}} \rangle \]  \hspace{1cm} (C.3)

To evaluate Eq. (C.3), we choose the coordinate axes so that the polar axis is along the vector \( \vec{k} \). If
denotes the angle between the vectors $\hat{R}$ and $\hat{K}$ then Eq. (C.3) can be written as,

$$S(\hat{R}, \hat{r}) = \frac{(kR)^2}{4\pi} \int \cos^2 \theta_{KR} e^{i \hat{K} \cdot \hat{r}} d\Omega_k$$

With the help of the addition theorem for spherical harmonic

$$\cos^2 \theta_{KR} = \frac{4\pi}{3} \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \frac{\ell^2}{2\ell+1} Y_{\ell m}(\hat{R}) Y_{\ell m}^*(\hat{r})$$

in which the spherical harmonics are referred to $\hat{r}$ as the polar axis. Integrating over $\phi_k$, and making use of the orthogonality property of the spherical harmonics, we obtain,

$$S(\hat{R}, \hat{r}) = \frac{2\pi}{3} (kR)^2 \sum_{\ell=0}^{\infty} \frac{\ell^2}{2\ell+1} \int_0^{\pi} \left[ Y_{\ell 0}(\hat{R}) Y_{\ell 0}^*(\hat{r}) e^{i k r \cos \theta_k} \sin \theta_k d\theta_k \right]$$

(C.4)

Using the relation $Y_{\ell 0} = \sqrt{\frac{2\ell+1}{4\pi}} P_{\ell}(\cos \theta)$ and changing the variable to $z = \cos \theta_k$, we arrive at,

$$S(\hat{R}, \hat{r}) = \frac{(kR)^2}{6} \sum_{\ell=0,2} \frac{\ell^2}{2\ell+1} P_{\ell}(\cos \theta) \int_{-1}^{1} P_{\ell}(z) e^{i k z \gamma} dz$$

(C.5)

The last integral has the following value,

$$\int_{-1}^{1} P_{\ell}(z) e^{i \mu z} dz = 2 i^\ell J_{\ell}(\mu)$$

(C.6)
Where $J_\ell(u)$ is the spherical Bessel function of order $\ell$.

From Eq.(C.5) and Eq.(C.6) it follows,

$$ s(\mathbf{R}, \mathbf{r}) = \frac{(kR)^2}{3} \sum_{\ell=0}^{\infty} i^\ell 2^{\ell+1/2} J_\ell(kr) P_\ell^0(\cos \theta_{RR}) $$ \hspace{1cm} (C.7)$$

For the nearest neighbors in the lattice the vectors $\mathbf{R}$ and $\mathbf{r}$ are mutually orthogonal. Thus if $R \neq r$ Eq.(C.7) simplifies to

$$ s(\mathbf{R}, \mathbf{r}) = \frac{(kR)^2}{3} [J_0(kr) + J_2(kr)] $$ \hspace{1cm} (C.8)$$

Similarly,

$$ s(\mathbf{r}, \mathbf{r}) = \langle (R \cdot r)^2 e^{i R \cdot r} \rangle = \frac{(kr)^2}{3} [J_0(kr) - 2J_2(kr)] $$ \hspace{1cm} (C.9)$$

From Eq.(C.2), Eq.(C.9) we finally have

$$ I(\mathbf{R}_i, \mathbf{R}_j) = \frac{k^2}{3} (\mathbf{R}_i \cdot \mathbf{R}_j) [J_0(kR_{ij}) + J_2(kR_{ij})] $$

$$ + \frac{k^2 R_{ij}^2}{4} J_2(kR_{ij}) $$

where $R_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$.

By making appropriate substitutions, we will obtain

$$ \langle (\mathbf{R} \cdot \mathbf{R}_i)^2 (\mathbf{R} \cdot \mathbf{R}_j)^2 \rangle = \frac{k^2}{3} (\mathbf{R}_i \cdot \mathbf{R}_j) $$

and

$$ \langle \mathbf{R} \cdot \mathbf{R}_i \mathbf{R} \cdot \mathbf{R}_j e^{i \mathbf{R} \cdot \mathbf{R}_j} \rangle = \frac{k^2}{3} (\mathbf{R}_i \cdot \mathbf{R}_j) [J_0(kR_j) - 2J_2(kR_j)] $$
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