Double Nuclear Quadrupole Resonance in Biological Compounds

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Abstract.

This thesis describes the mechanisms, applications and limitations of the technique of nuclear quadrupole resonance carried out using double resonance with spin mixing in the laboratory frame.

In the first chapter the basic elements of the theory of quadrupole resonance are outlined and the quadrupole Hamiltonian is solved for spin 1 nuclei. The second chapter describes some of the ways in which quadrupole parameters may be used to extract information about the electronic structure of molecules.

In chapter III the most common techniques for the measurement of $h_{QK}$ are discussed and some of their advantages and limitations are noted. The next two chapters give a detailed description of the technique of double resonance with spin mixing in the laboratory frame as applied to nitrogen and deuterium nuclei. The events of an experimental cycle are related and the layout of the apparatus is presented. The inherent high sensitivity of the method is attributed to the large population differences given to the quadrupolar nuclei by level crossing processes with the protons. For nitrogen, a simple model where the protons transfer alignment in mutual spin flip transitions involving a single proton and a single nitrogen is shown to predict a lower sensitivity for the technique than that found experimentally. The relative sensitivities to the three transitions in nitrogen NQR, as predicted from the simple model, are in qualitative agreement with experiment.

In chapter VII the solid effect transitions occurring when
a nitrogen is bonded to one, two, or three protons are discussed. The energy of the two proton system, which determines the frequencies of $NH_2$ solid effect transitions, is solved as a function of applied magnetic field.

The fine structure in deuterium pure quadrupole resonance, which occurs when nearby deuterons have nearly degenerate energy levels, is theoretically analysed in chapter VIII. The heights of the subsidiary lines in the fine structure are predicted and the quadrupole lines are assigned from a calculation of the magnetic dipolar interaction between the two nearby deuterons. In chapter IX, the characteristics of the quadrupole spectra from OHD and NHD sites have been qualitatively accounted for by attributing them to the magnetic dipolar interaction between the deuteron and the proton.

Since this technique is quite new and the methods of running the apparatus and interpreting the spectra have not yet become well established, a fairly detailed section on operational procedures and the assignment of nitrogen and deuterium quadrupole lines has been included.

In the literature there has been some controversy over the assignment of quadrupole constants to the two nitrogen sites in imidazole. In chapter XI the set of lines with $e^2 qQ = 1418$ KHz and $\eta = 0.997$ is positively assigned to the NH site and the $e^2 qQ = 3233$ KHz and $\eta = 0.135$ to the N with no covalently bonded protons.

In chapter XII the quadrupole resonance technique is applied to the study of hydrogen bonding in amino acids. Three relations of the form $e^2 qQ = (e^2 qQ)_0 - A/R(H...O)$ have
been found. \((e^2 qQ)_0\) represents the \(e^2 qQ\) of a non-hydrogen bonded site. For O-D...O bonds \((e^2 qQ)_0\) and \(A\) were found to be 328 KHz and 643 KHz-angstrom\(^3\). The OD\((e^2 qQ)_0\) is in good agreement with experimentally determined values. For N-D...O and N\(^4\)D...Cl bonds the values were 252 KHz and 572 KHz-angstrom\(^3\) and 239 KHz and 728 KHz-angstrom\(^3\). The average \((e^2 qQ)_0\) value for a non-hydrogen bonded N\(^4\)D is in excellent agreement with that predicted by a theoretical calculation in the literature.

The quadrupole resonance of the water molecule has been carried out in a number of different environments including ice Ih, ice II, clathrate hydrates and molecular complexes. The ice Ih spectrum has been shown to be the sum of two components, one from the HDO molecule and the other from the D\(_2\)O molecule.

Although this thesis is largely devoted to the quadrupole resonance of \(^{15}\)N and \(^2\)H, a preliminary research project was undertaken to apply the technique to a number of different nuclei with quadrupole transitions in the frequency range around a few MHz. This project was quite successful with quadrupole resonance having been observed in \(^{23}\)Na, \(^{39}\)K, \(^{12}\)C, \(^{17}\)O, \(^{27}\)Al and \(^{10}\)B. This quadrupole data, along with the solutions of the quadrupole Hamiltonian for spins \(\frac{3}{2}, \frac{5}{2}\) and \(3\) is written up in chapter XIV. Because the processes of laboratory frame double resonance depend on the nuclear spin and the quadrupole frequencies, the observations in chapter V on the mechanisms of the method for nitrogen and deuterium resonance do not necessarily apply to the new nuclei.
A comprehensive list of quadrupole data for nitrogen and deuterium is presented in appendices I and II.
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Introduction.

Any nucleus with nuclear spin I > 1 undergoes an orientation dependent interaction with the local electric field gradient. The measurement of this interaction which occurs between the quadrupole moment of the nucleus and the electric field gradient at a nuclear site is known as nuclear quadrupole resonance. The magnitude and direction of the electric field gradient at a nuclear site are very dependent upon the particular bonding configurations at the site so, from quadrupole resonance experiments, information obtained about the electric field gradients can yield an important insight into the electronic structure of molecules.

The first successful NQR experiment in the solid state was carried out by H.G. Dehmelt and H. Kruger in 1951 (1). Since then NQR has become an established spectroscopic technique and it has been applied to a large number of nuclei. NQR spectroscopy spans the vast frequency range from ~10 KHz to 1000 MHz but due to experimental convenience a large proportion of the total of NQR data has, in the past, been collected on the halogens and other nuclei with relatively high transition frequencies.

Recently, a number of new double resonance techniques, pioneered by E.L. Hahn, have made it possible to measure quadrupole splittings with high sensitivity in the frequency range around 1 MHz. An apparatus employing one of the simplest of these NQR techniques, known as double resonance with spin mixing in the laboratory frame, has been built in the Clarendon Laboratory by Dr. D.T. Edmonds. This thesis discusses some of the principles, advantages and limitations
of this technique and, hopefully, demonstrates its practicability for a wide range of problems. Most of this thesis is directed onto the NQR of nitrogen 14 and deuterium nuclei since these nuclei are particularly well suited to investigation by the laboratory frame double resonance technique and they are very commonly found in compounds of interest to biology.
Chapter I. Introductory Quadrupole Resonance Theory.

In this chapter the basic elements of the interaction of a nucleus with an electrostatic field will be considered. Since this topic is treated in detail in references (2, 3, 4) only a brief outline will be presented here.

Classically the energy $E$ of a nucleus with charge distribution $\rho(r)$ in a potential $V(r)$ due to other sources is given by

$$E = \int \rho(r) V(r) d\gamma$$

If $V(r)$ is expanded in a Taylor series about the origin this becomes

$$E = V(0) \int \rho(r) d\gamma + \sum \left[ \frac{V}{2!} \int \rho(r) d\gamma \int \frac{V}{2!} \int \rho(r) d\gamma + \sum \frac{V}{2!} \int \rho(r) d\gamma \int \frac{V}{2!} \int \rho(r) d\gamma \right]$$

+ terms of higher order

The first term of this expansion is a scalar independent of the size or shape of the nuclear charge distribution and it may be neglected in a quadrupole resonance consideration. The second term involves the electric dipole moment of the nucleus. Because the wave function describing the nucleus in its ground state possesses a definite parity, the nuclear charge distribution can be shown to have inversion symmetry (4). Then the integral $\int x_0 \rho(r) d\gamma$ must vanish so the nucleus cannot have an electric dipole moment and the second term is zero. (Some recent nuclear models do predict a very small electric dipole moment for some nuclei but the electric dipole energy would still be negligible (2)). Then the lowest order nuclear orientation dependent term in the electrostatic energy of the nucleus is the third term known as the electric quadrupole energy. The quadrupole energy is the product of two quantities: the electric field
1.2

gradient elements \( \nabla_{i} \nabla_{j} = \sum_{k} \frac{\partial^{2}}{\partial x_{i} \partial x_{j}} \delta_{k_{i} k_{j}} \) and the nuclear quadrupole moment \( \int x_{i} x_{j} \rho(r) d\gamma \).

The electric field gradient is characterized by a 3 x 3 symmetric tensor, which, in its principal axis system, contains only three elements \( V_{xx}, V_{yy}, V_{zz} \). If electric charge at the nucleus due to spherically symmetric 5 electrons is neglected (the electric field gradient at the centre of a spherically symmetric charge distribution is zero) Poissons equation may be applied:

\[ \nabla^{2} V = V_{xx} + V_{yy} + V_{zz} = 0 \]

therefore the electric field gradient tensor is determined by specifying the direction of its principal axes and any two of its elements in the principal axes system. By convention the principal axes of the electric field gradient are labelled such that \(|V_{zz}| \geq |V_{yy}| \geq |V_{xx}| \). The quantity:

\[ \eta = \frac{|V_{yy}|}{|V_{zz}|} - \frac{|V_{xx}|}{|V_{zz}|} \]

which may have values from zero to one is called the asymmetry parameter. The asymmetry parameter \( \eta \) and \( z \) component of the field gradient \( q = V_{zz}/e \) are customarily used to define the field gradient tensor.

The quadrupole moment term \( \int x_{i} x_{j} \rho(r) d\gamma \) is also a 3 x 3 symmetric tensor and it can be made traceless by the addition of a spherically symmetric quantity. It may be written in a convenient quantum mechanical form \((2,4)\) by replacing \( \rho(r) \) with an operator which depends on the position vectors of the nucleons in the nucleus and making a change of variables from the radius vector \( r \) and its coordinates \( x, y, z \) to the total nuclear spin \( I \) and the magnetic quantum numbers \( m \) denoting its orientation, with
these changes and some algebraic manipulation the quadrupole Hamiltonian can be put into the form:

\[ H_Q = \frac{eQ}{2\hbar(2I-1)} \left( V_{xx} I_x^2 + V_{yy} I_y^2 + V_{zz} I_z^2 \right) \]

or in terms of \( \eta \) and \( q \) and the raising and lowering operators:

\[ H_Q = \frac{e^2 q Q}{4\hbar(2I-1)} \left( 3I_x^2 - I_z^2 + \eta^2 (I_+^2 + I_-^2) \right) \]

The quantity \( Q \) is conventionally called the nuclear electric quadrupole moment and is defined by:

\[ eQ = \int \rho_{II}(r) (3z^2 - r^2) \, d\gamma \]

where \( \rho_{II}(r) \) represents the expectation value of the nuclear charge density in the state where \( m = 1 \). \( eQ \) is a measure of the deviation of the nuclear charge distribution from spherical symmetry; for a prolate spheroidal distribution \( Q \) is positive and for an oblate spheroid \( Q \) is negative.

Since most of the research to be described in this thesis involves nitrogen \( ^{14} \) or deuterium the quadrupole Hamiltonian will be solved here for the case of nuclear spin \( I = 1 \). If there is no external magnetic field and dipolar interactions with other nuclei are assumed negligible, a spin 1 nucleus in a molecular crystal will have eigenstates determined by the quadrupole Hamiltonian. In terms of magnetic spin states \( | -1 \rangle , | +1 \rangle \) and \( | 0 \rangle \) taken along the principal axes of the electric field gradient the Hamiltonian may be written:

\[ H_Q = e^2 q Q \left( \begin{array}{ccc} 1 & \eta & 0 \\ \eta & 1 & 0 \\ 0 & 0 & -2 \end{array} \right) \]

This may be diagonalized by a rotation about the z axis obtaining

\[ H_Q = e^2 q Q \left( \begin{array}{ccc} 1-\eta & 0 & 0 \\ 0 & 1+\eta & 0 \\ 0 & 0 & -2 \end{array} \right) \]
1.4

with eigenstates labelled $|B\rangle$, $|A\rangle$, $|0\rangle$ where $|B\rangle = \frac{1}{\sqrt{2}} (|\uparrow\rangle - |\downarrow\rangle)$, $|A\rangle = \frac{1}{\sqrt{2}} (|\uparrow\rangle + |\downarrow\rangle)$, and $|0\rangle = |0\rangle$. These states transform under rotations in an analogous way to the electronic wave functions i.e., $|B\rangle$, $i|A\rangle$, $|0\rangle$ transform like $x, y, z$.

On the application of an oscillating magnetic field of the appropriate frequency there are three allowed magnetic dipole transitions labelled $V_+$, $V_-$ and $V_0$ (electric dipole transitions cannot occur because the nucleus does not have an electric dipole moment).

<table>
<thead>
<tr>
<th>Transition</th>
<th>States involved</th>
<th>Energy splitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_+$</td>
<td>$</td>
<td>A\rangle \leftrightarrow</td>
</tr>
<tr>
<td>$V_-$</td>
<td>$</td>
<td>B\rangle \leftrightarrow</td>
</tr>
<tr>
<td>$V_0$</td>
<td>$</td>
<td>A\rangle \leftrightarrow</td>
</tr>
</tbody>
</table>

The transition probabilities are proportional to $|\langle \text{final state} | \frac{I}{\text{H}} | \text{initial state} \rangle|^2$ and are listed in the following table for oscillating fields $H_{\gamma}$ along the principal axes directions.

<table>
<thead>
<tr>
<th>direction of $H_{\gamma}$</th>
<th>$V_+$</th>
<th>$V_-$</th>
<th>$V_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\hat{x}$</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\hat{y}$</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>$\hat{z}$</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

Then, for a single crystal, by changing the direction of $H_{\gamma}$ the principal axes of the electric field gradient tensor may be obtained while for a powder sample - the case for all experiments described in this thesis - the transition probabilities for the three transitions are equal.

If a magnetic field is applied, the total Hamiltonian for an isolated spin 1 nucleus in an electric field gradient is $\hat{H}_Q + \hat{H}_Z$ where $\hat{H}_Z = \frac{3}{2} I_3 H_{\gamma}$. In terms of the $|B\rangle$, $|A\rangle$, $|0\rangle$ states, for a magnetic field at $\theta, \phi$ to the electric field gradient principal axes the Hamiltonian becomes
For this Hamiltonian, if $\eta$ is non-zero and $R \ll 1$ the energy eigenvalues are independent of $H$ to first order, in fact \( \frac{\partial H}{\partial H} = 0 \). This phenomenon is called quenching—the magnetic field interaction is said to be quenched by the quadrupole interaction. Spectroscopy carried out in this case is called nuclear quadrupole resonance (NQR). It is interesting to note that if $\eta$ is zero the $z$ component of the magnetic field interaction will be on the diagonal and there is no quenching. This effect becomes less pronounced as $\eta$ increases from zero.

If $R \gg 1$ the Hamiltonian will be diagonalized with base states $|+\rangle, |-\rangle, |0\rangle$ along the magnetic field by $\hat{H}_z$ and $\hat{H}_Q$ will act as a perturbation on the energy eigenvalues. Spectroscopy carried out in the high magnetic field region is called nuclear magnetic resonance (NMR).

If a small magnetic field is applied its contribution to the energy eigenvalues may be calculated using perturbation theory. The quadrupole energy levels will in general be shifted and the direction of the shift will depend on the angle between the magnetic field and the field gradient axes. Megata (5) has made this calculation for a powder sample containing spin 1 nuclei. He found that small fields broadened and shifted $\nu_+ \times$ lines in the direction of increasing frequency and broadened and shifted $\nu_-$ lines in the direction of decreasing frequency. This feature is very helpful experimentally in identifying $\nu_+ \times$ and $\nu_-$ lines in complex spectra.
Chapter II. Interpretation of the Quadrupole Constants.

As described in the previous chapter, a quadrupole resonance experiment on a powder sample containing spin 1 nuclei gives two independent parameters $e^2 q Q$ and $\eta$ characterizing the electric field gradient at the nuclear site. These parameters will now be discussed in more detail.

$e^2 q Q$ is the product of two quantities, the nuclear electric quadrupole moment, $eQ$, and the $zz$ principal component of the electric field gradient tensor $e\omega$, being a property of the nucleus alone, is the same for all compounds in which a given nucleus occurs (provided the nucleus remains in its ground state). Then, if a series of quadrupole resonance experiments are performed on the same nucleus, e.g. nitrogen, and only relative values of the electric field gradient are desired it is unnecessary to know the value for $eQ$. Often this is the case, however if calculated electric field gradients are to be compared with experiment it is important to have an accurate value for $eQ$. Unfortunately, in general, quadrupole moments are not known very accurately. Whereas magnetic dipole moments can be determined precisely since it is easy to apply a magnetic field larger than internal fields, the electric field gradient at a nuclear site is higher than it would be practicable to produce in the laboratory (nuclear field gradients are of the order $10^5$ statvolts/cm whereas the gradient at which air ionizes is of order $10^6$ statvolts/cm. It may be possible to apply much higher field gradients in a vacuum). Nuclear shell model treatments (6) can account for the
II.2

behaviour of $eQ$ as a function of the number of protons and neutrons but they do not generally give results for a particular nucleus which are as accurate as those deduced from calculations of electric field gradients. The current accepted values for quadrupole moments of nitrogen ($\pi$) and deuterium ($\xi$) have been obtained by comparing values of $eQ$ from ab initio electronic wave functions in simple compounds with experimental values of $e^2q_\xi$.

The calculation of $eQ$ at nuclear site $A$ involves the following expression

$$
eQ = e \left[ \sum_{B \neq A} Z_B \left( \frac{3 \cos^2 \Theta_{AB} - 1}{R_{AB}^3} \right) - \int \sum_{k=1}^{n} \left( \frac{3 \cos^2 \Theta_{Ak} - 1}{r_{Ak}^3} \right) \Psi^* \Psi \ d\gamma \right] \quad \text{II.1}
$$

where the first sum is over nuclei $B$ and the second over electrons $k$. The $\Theta$'s are the angles between the $z$ principal axis of the field gradient and the radius vectors $R_{AB}$ from nucleus $A$ to nucleus $B$ and $r_{Ak}$ from nucleus $A$ to electron $k$ (if the principal axes are unknown they may be found by calculating all the elements of the field gradient tensor with sums similar to eqn (1) and diagonalizing it). The molecular wavefunction $\Psi$ represents the distribution of electronic charge as a function of position. $\Psi$ can be expressed as a set of molecular orbitals, each consisting of a combination of orthogonal orbitals about a particular centre.

The calculation of the first term in eqn II.1 is a simple electrostatic sum over nuclei although in a very accurate treatment a consideration of nuclear vibration may be included. In the second term of eqn II.1 three types of integrals of increasing complexity may arise - integrals involving a common origin, those about two different
II.3

centres and those about three different centres. The calculation of field gradients is reviewed in reference (9).

Then, knowledge of the electronic wavefunction and the molecular structure is all that is necessary to obtain eq. However, at present, accurate wave functions are known only for a few relatively simple molecules and, unfortunately, the production of molecular wavefunctions becomes much more difficult when the molecules are bonded together in crystals. An important function of the measurement of quadrupole constants is to provide a sensitive check on the precision of newly calculated molecular wave functions.

Qualitative estimates of the quadrupole parameters can be made very easily. For example, from the definition of \( \eta \) it can be clearly seen that a charge distribution of axial symmetry (i.e. \( V_{xx} = V_{yy} \)) will have an \( \eta \) of zero. Although it is not so obvious, it is not difficult to show that a tetrahedral hybridization scheme with two pairs of hybrids with equal electron occupation exhibits an \( \eta \) of 1. From a very basic model where the electronic charge distribution is simulated by a set of point charges with the same geometry, Bancroft and Platt (10) have calculated the quadrupole constants in terms of hybrid occupations for a considerable number of hybridization schemes. Although this type of calculation is very qualitative it can be of assistance in assigning measured quadrupole lines to inequivalent sites. A. J. Hunt, a colleague, has predicted (11), using a point charge model, that in a tetrahedral hybridization scheme small changes in hybrid occupation (such as the occurrence of hydrogen-bonding) have a larger
II.4

effect on the value of $\eta$ when $\eta$ is near 0 than when it is close to 1. This has been confirmed experimentally.

Several approximate methods have been devised to extract information about electronic structure from the quadrupole constants. One of these which has been frequently applied to nitrogen is called the Townes and Dailey method (12).

The electric field gradient at a nuclear site in a molecule may be attributed to three sources: the electrons and nuclei belonging to neighboring atoms; the inner core of closed shell electrons surrounding the nucleus; and valence electrons which have a high probability of being close to the nucleus. The essence of the Townes and Dailey method is to distinguish which of these contributions are most significant and which may be neglected in a semi-quantitative treatment.

Townes and Dailey calculate that an electron 1 angstrom away from a nitrogen nucleus should cause only about 10% as large a field gradient as that from a 2p electron. Furthermore nuclei and electronic charge from a neighboring atom should have cancelling effects so they are assumed not to have a significant effect on the field gradient. Subsequent molecular orbital calculations on some simple molecules (9 page 124) have shown this to be approximately true.

Closed shell orbits, in nitrogen the 1S and 2S, are assumed to be accountable for less than 10% of the field gradient. This is not a universally applicable assumption; in some ions distortions of closed shells result in field gradients which are more than an order of magnitude larger.
than they would be if the shells were spherically symmetric. However, this effect, known as Sternheimer shielding (2), is small for nitrogen in molecular crystals.

If neighbouring atoms and closed shell electrons are neglected, then the valence electrons must be responsible for the major part of the nitrogen field gradients. Townes and Dailey estimate that the 2p electrons of nitrogen can to an accuracy of the order of ten percent be treated as the sole contributors to the electric field gradient.

It is very simple to carry out a Townes and Dailey analysis on a covalently bonded nitrogen. A set of four orthogonal hybrid orbitals made up of the appropriate linear combinations of S and P orbitals are chosen to represent the nitrogen hybridization scheme. An electron occupation is assigned to each hybrid orbital and a simplified version of eqn II.1 including the Townes and Dailey assumptions is used to calculate the field gradient in units of eq. - the field gradient produced at the nucleus by one 2p electron. Using the accepted value for eq (e^2 q, ~ 1.5 x 10^-2 for an uncharged nitrogen), a relation is found between the four bond occupations and the two experimentally determined quadrupole constants. This is clearly not enough information to determine the distribution of electrons among the orbitals but if some further assumptions are made - for example, non bonding orbitals (lone pairs) may be assigned two electrons occupation and identical bonds may be given the same occupation - it is possible to obtain absolute bond occupations. In view of the approximations made, the Townes and Dailey method is not particularly accurate but
it is useful in observing trends of electronic distribution in similar nitrogen compounds. An example of a simple Townes and Lailey analysis of nitrogen compounds is found in reference (13).

Clearly the Townes and Dailey method cannot be applied to deuterium electric field gradients since the only electron with an orbit centred on the nucleus is in a spherically symmetric 1s orbital. The assumptions used for nitrogen that the neighbouring nuclei and electrons cancel with each other is no longer valid. In fact it has been found from molecular orbital calculations on C2 bonds in several simple molecules (14) that the electric field gradient at the deuterium nucleus is produced chiefly by nuclear and electronic charge centred on the carbon atom. Because the positive contribution from the carbon nucleus and the negative contribution from electrons centred on the carbon are both large and of the same order of magnitude the resultant field gradient is very sensitive to small changes in either.

Since the source of the electric field gradient at a deuteron is along its covalent bond it is not surprising that deuterium $\eta$'s are rarely larger than 0.2 and that the z principal axis of the electric field gradient is almost always within a few degrees of the covalent bond direction. (An exception occurs when the deuteron undergoes a rapid oscillation between two or more sites. Then an averaged field gradient is measured and this can have large values of $\eta$ and a z principal axis not along the bonds (15)).
Chapter III. Measurement of Quadrupole Resonance.

A variety of experimental techniques are available for the detection of quadrupole resonance in molecular crystals in the frequency region around 1 MHz. The advantages and limitations of some of these methods will be discussed briefly in this section.

A large proportion of $^{14}$N quadrupole resonance data from molecular crystals has been obtained by continuous wave methods. There are several types of continuous wave methods but basically they involve the detection of a change in the resonant impedance of a tank circuit when the resonant frequency of the circuit coincides with a quadrupole resonance in the sample which is contained inside the inductance of the circuit. The applied magnetic field is usually zero or very small compared with the quadrupole splittings so the nuclei are in quadrupole eigenstates. Unfortunately, a large number of nitrogen compounds are not amenable to CW resonance techniques due partly to the difficulty of avoiding saturation of the energy levels (long $T_1$ s) and partly to a poor low frequency response. Frequencies below 1 MHz are practically unobtainable and since most nitrogen $v_o$ transitions occur below 1 MHz, in general only $v_+^\prime$ and $v_-$ can be detected in nitrogen compounds. However continuous wave techniques are simple to set up experimentally and with a single crystal sample the principal electric field gradient axes may be obtained. Deuterium quadrupole resonance cannot be carried out with continuous wave techniques because of the low frequencies involved.

It is possible to measure nitrogen quadrupole resonances
by observing the free induction decay or spin echo following
the application of high power radio-frequency pulses at the
quadrupole frequencies (17). This is similar to the pulsed
magnetic resonance techniques and is also especially applic­
able to the measurement of relaxation times. Pulsed NQR
is not beset by the saturation problems of continuous wave
NQR but good resolution is possible only at frequencies above
0.5MHz so it cannot measure deuterium resonance.

Before the introduction of the double resonance tech­
niques practically all the measurements of deuteron quad­
rupole constants were made by nuclear magnetic resonance.
With NMR the quadrupole interaction of the nucleus is ob­
served as a perturbation on the energy levels of the nuclear
magnetic moment in a large applied magnetic field. Because
deuteron $e^2\tilde{Q}$'s are small the condition $\gamma_1\ll e^2\tilde{Q}$ can be
satisfied with moderate magnetic fields ($\sim 15$ kGauss).
However, for $^{14}N$ magnetic resonance very high fields are
necessary if the eigenstates of the nitrogen nuclei are to
be determined by the magnetic field. If single crystals are
used NMR can yield very accurate quadrupole parameters and
also the principal axes of the electric field gradient.
However, the spectra of single crystals can be very tedious
to resolve since crystallographically equivalent sites will
give different spectra if they have different orientations
relative to the applied magnetic field. It is practical to
do NMR of deuterium on powder samples (14, 18) but the quad­
rupole lines are broader than in single crystals and deduc­
tions of $\eta$ are less accurate. Deuteron magnetic resonance
has been carried out on molecules oriented by a nematic
liquid crystal solvent (19) but this measurement provides only the field gradient component along a symmetry axis of the molecule and does not give a value for $\gamma$.

In the past decade a number of double resonance methods have evolved which, for a restricted class of compounds, can measure quadrupole resonance with very high sensitivity (20). For a compound to be amenable to these double resonance techniques it must contain in addition to the quadrupolar nucleus of interest, labelled the $B$ nucleus, a second type of nucleus, the $A$ nucleus, which has an easily measurable magnetization. Furthermore, there must be some interaction (e.g., magnetic dipolar) between the two types of nuclei. At least three fundamentally different double resonance techniques have been used to measure quadrupole resonance.

In one technique called INDOR changes are observed in the linewidth of the nuclear magnetic resonance signal of the $A$ nuclei when transitions are induced in the $B$ nuclei by the application of an oscillating field at a quadrupole resonance frequency. This method is described in reference (21).

Double resonance with spin-mixing in the rotating frame is a powerful method which can detect resonance with very low concentrations of quadrupolar nuclei. The experiment is carried out with the sample in a large applied magnetic field. By equalizing the Zeeman energies of the $A$ and $B$ spin species in their respective rotating frames cross-relaxation is achieved between the two species. In this manner, a small number of $B$ nuclei being irradiated at
their resonant frequency can effect a considerable decrease in the population difference of the A nuclei. Then, by measuring the alignment of the A spins it can be established whether or not the B system has undergone a quadrupole resonance. A serious disadvantage of this technique is the requirement of single crystal samples. In a variation of this technique, where the cross-relaxation takes place in zero external magnetic field by matching the B system rotating frame Zeeman energy with the energy of the A nuclei in their local fields (22), single crystals are not required.

The NQR technique used for the research in this thesis is called double resonance with spin mixing in the laboratory frame (23). In this method, which will be described in detail later, the cross-relaxation is achieved by instantaneously equalizing the energies of the A and B nuclei in an applied DC magnetic field but the B nuclei are irradiated with a low power radio frequency field in a region of zero applied DC magnetic field. Laboratory frame double resonance is not generally so sensitive to low abundances as rotating frame double resonance but there are no requirements on the power of the r.f. field and single crystals are unnecessary unless the directions of the field gradient tensor are required.
Chapter IV. Laboratory Frame Double Resonance - Introduction and Apparatus.

The laboratory frame double resonance apparatus used for the research in this thesis has proved itself very practical for measuring the $J<k$ of $^{14}N$ and $^2H$ as well as a number of other nuclei. In this chapter the details of the apparatus and the method shall be outlined in preparation for the next chapter where the method and the reasons for its high sensitivity will be discussed.

In all the measurements carried out with our apparatus protons have been used for the $\alpha$ nuclei. Protons are an obvious choice since they have a large magnetic moment and they are abundant and can interact with nitrogens and deuterons in most organic molecules. Due to the large proton magnetic moment the energy splitting between the two proton spin states for magnetic fields greater than a few kilogauss is much larger than any of the quadrupole splittings to be measured. On the other hand in zero magnetic field the protons are aligned along the dipolar fields of neighbouring protons and their energy splitting is usually smaller than that between any two quadrupole states in nitrogen 14 samples or that between the more widely split states in deuterium samples. Then, at intermediate fields the proton energy splittings can become equal to those in the quadrupolar nuclei and when this happens dipolar interaction between the two spin species induces mutual spin flips. This process involves no net change in energy but in equilibrium the ratio of the populations of the upper and lower states of the protons is equal to that
of the two levels involved in the quadrupolar nuclei. By this process, called level crossing, alignment in the protons can be transferred to the quadrupolar nuclei.

In our laboratory frame double resonance experiment a quadrupole spectrum is produced in a series of cycles, one cycle for each frequency sampled in the spectrum. The cycle begins by holding the sample in a magnetic field of 7 kilogauss until the protons have reached equilibrium alignment (i.e. a Boltzmann distribution). This time, which depends on the spin-lattice relaxation ($T_1$) of the protons in the sample, is typically a few minutes. The sample is then removed to a position where the magnetic field is zero. During the removal from the high field the energy splitting between the two proton spin states will decrease from about 30 MHz to a few MHz. The quadrupole split levels will successively, from the largest to the smallest, be matched by the proton levels and level crossings will take place so the quadrupolar nuclei will be given a higher alignment than they could have achieved in equilibrium with either the high field or the zero field. While the sample is in the zero field region a radio frequency field is applied to it. If the frequency of the field coincides with a quadrupole resonance some of the alignment in the quadrupolar nuclei will be destroyed. After a few seconds of irradiation the sample is returned to the high magnetic field and once again level crossings occur; this time the smaller quadrupole splittings level cross with the protons before the larger quadrupole splittings. The final proton magnetization, the magnitude of which will depend on
Figure IV 1 Sequence of events in one cycle of the experiment

H = 0
Homolax coils

H = 7 Kg
Permanent magnet

Protons attain equilibrium alignment in the high magnetic field.

Level crossing: Protons transfer their alignment to the nitrogens.

Remaining proton magnetization decays; nitrogens are irradiated at some frequency in their quadrupole spectrum.

Level crossing: Protons magnetization the next cycle is measured by 90° pulse and recorded.

Extent of realignment of the protons is a function of the nitrogen alignment at the end of the uptime.
whether or not a quadrupole resonance was excited in the zero field region, is now measured, completing the cycle. The entire cycle is repeated, each time with an incremented frequency of quadrupolar irradiation until the spectrum is complete. To ensure reproducibility the proton magnetization is reduced to zero at the beginning of each cycle.

To make the writing less clumsy the locations of the magnet pole gap and the quadrupolar irradiation coil shall henceforth be labelled position 1 and position 2. The period of time the sample spends in position 1 shall be called the 'downtime' and duration in position 2 the 'uptime'. The names 'uptime' and 'downtime' have evolved because in our apparatus position 2 is located directly above position 1.

The experiment is carried out in the inner chamber of a dewar system consisting of three concentric chambers. The outer chamber is maintained at a very low pressure to ensure thermal insulation and a liquid refrigerant is poured into the central chamber. Most of the experiments are carried out at 77K using liquid nitrogen but liquid hydrogen (20K) has been used and the apparatus may be run at room temperature. The inner chamber of the dewar, containing the sample, is filled with helium gas which functions as a thermal exchange gas. The sample which may be a powder or a frozen liquid is contained in a 5 ml PTFE container. This container is attached to a metal rod which can move it between the two positions - position 1 between the poles of a 7 kilogauss permanent magnet and position 2, 60 cm above the magnet pole gap, where the magnetic field is bucked to zero by a pair of Helmholtz coils. If required,
these Helmholtz coils can apply DC magnetic fields up to about 70 gauss to the sample. The metal rod which holds the sample container is linked through a set of pulleys to a piston that can move up and down in a sealed tube under the pressure from the compressed air line. Then, by electronically controlling a set of valves which determine the direction of air pressure inside this tube, the sample can be moved back and forth between positions 1 and 2.

At position 2 there is a second set of coils which are used to apply a radio-frequency field in the quadrupolar spectrum. A frequency synthesiser which can be programmed by a digital control box is connected to a broad band power amplifier to produce an r.f. field at position 2 of amplitude up to about 15 gauss peak to peak through most of the frequency range of 1 KHz to 3 MHz. The frequency of the r.f. field may either be constant or it may be stepped through a range of values during the uptime.

At the end of each cycle the proton magnetization is measured by applying a 90° pulse and observing the free induction decay. This is accomplished with a single coil pulsed NMR spectrometer similar to that described in reference (24). The problem in the design of a single coil pulse spectrometer is that, while for the duration of the 90° pulse a voltage of order 1000V is applied across the sample coil, after a time short compared with the proton spin-spin relaxation time $T_2$, an induced nuclear signal of the order of a few millivolts must be detected by the same coil. This feat is achieved with a special arrangement of matched transmission lines and non linear diodes which
Figure IV 2 Block diagram of the apparatus
IV.5

isolate the receiver from the circuit during the 90° pulses and isolate the transmitter during the signal detection process.

The sample coil is a simple tank circuit (described in (24)) with a relatively low 'Q' value in order to lower its dead time. The transmitter layout follows that in reference (25). It produces 30 MHz pulses of duration about 3 μsec for the 90° pulse. The free induction decay can be tuned (i.e. the proton Larmour frequency set to the 90° pulse frequency) by adjusting the LC current in a pair of coils aligned across the pole gap of the permanent magnet.

The sample container and the cylinder on which the sample coil is wound are made from TiJ which contains fluorine nuclei. The fluorine nuclei, which have a high field splitting of 32 MHz compared with the proton splitting of about 30 MHz, produce a free induction decay that turns out to be considerably larger than that from the protons. This creates the problem for the receiver that the two types of signal have to be separated and that, before separation, to amplify the proton signal to an acceptable value may result in overloading the amplifiers with the larger fluorine resonance. The induction signal from the coil is first led into a tuned 30 MHz preamplifier with a gain of about 200. It is then amplified again by a broad band amplifier with a gain of about 60. The broad band amplifier is protected from the large pulse transient at the beginning of the induction decay by a blocking pulse. The proton signal is now separated from the fluorine signal by a phase-sensitive detector, then the free induction decay envelope is recorded.
on a digital transient recorder. An output of the transient recorder memory is displayed on an oscilloscope and a portion of it is sampled by a gated integrator and plotted on a chart recorder. The product of a quadrupole resonance experiment is a chart recorder plot of proton magnetization at the end of a cycle as a function of the frequency of irradiation during the uptime.
Figure IV.3 Chart recorder plot of acetamide deuterium V. lines.
Chapter V. Laboratory Frame Double Resonance - Mechanisms and Sensitivity.

The current understanding of the processes involved in the double resonance with spin mixing in the laboratory frame technique shall now be presented. This treatment shall be restricted to spin 1 nuclei since most of the research has been on nitrogen 14 and deuterium. Because the frequency ranges of their quadrupole spectra are different, nitrogens and deuterons are affected differently by their interaction with the protons and they must be considered separately. Here, nitrogen NQR shall be discussed first and then the points where deuterium NQR varies will be examined.

The sensitivity and the applicability of the laboratory frame double resonance method depends critically on the relaxation times of the spins involved. If the spin-lattice relaxation time $T_1$ of the protons in the high field is not in the range 5 sec to several minutes AQR is impossible. For very short $T_1$'s the protons instantly lose any alignment transferred to them by the nitrogens, and for very long $T_1$'s the length of time required to have a proton magnetization build up in position 1 is impractically long. The value of the proton $T_1$ in zero field can be as much as an order of magnitude shorter than that in the high field but the sensitivity of the apparatus to nitrogen NQR is generally independent of the proton zero field $T_1$ (this will be discussed later).

In most of the samples used here the free induction decay of the protons had a time constant in the range 5 to 15 $\mu$sec.
In a spin echo experiment one sample, glycine, was found to have a spin-spin relaxation time $T_2$ of about 12 μsec, only a few μsec longer than its free induction decay. This evidence and also the fact that there is a range in free induction decay lengths supports the assumption that proton $T_1$'s are not much longer than the time constants of their free induction decays. The only requirement on $T_1$, that it be longer than the dead time of the signal detection system, has always been satisfied.

When, as is the case here, $T_1$ is much longer than $T_2$, in a time a few $T_2$'s after a disturbance in population the protons adopt an equilibrium temperature throughout the sample which tends toward the lattice temperature with a rate $T_1$. For times greater than $T_2$ after a population disturbance the protons are often referred to as a spin bath. In some exceptional samples, the presence of very inhomogeneous environments, such as paramagnetic impurities or 'islands' of protons isolated from other protons by large internuclear distances or crystallite boundaries, different protons may have different $T_1$'s and the spin bath only exists among a group of interacting protons.

Nitrogen nuclei, having three energy levels, exhibit three relaxation times - one for each transition - making experimental measurement of $T_1$'s more complicated. However, in this treatment it is sufficient to define a different time constant which describes the rate at which the magnetization passed on to the protons by the nitrogens in a cycle (without quadrupole irradiation) decreases as the sample spends longer in position 2. This time is experi-
mentally found to be several minutes for most samples at 77K. If it were less than a few seconds nitrogen NQR would be impossible since the nitrogens must retain some population difference in the absence of irradiation. If, in zero field, the nitrogens have energy level splittings comparable with those of the protons they can undergo cross-relaxation with the protons. The details of this will be discussed later.

Since the nitrogens are quenched by their quadrupole interaction and are usually fairly widely spaced in the crystal, they should have little interaction with each other and hence show long T_2's. The lower limit on T_2, set by the quadrupole line widths, is of the order of a millisecond.

These relaxation times, especially the proton T_1's, can vary considerably with temperature.

The cross-relaxation occurring between the protons and nitrogens when their energy level splittings are nearly equal (or if a nitrogen splitting is a multiple of the proton splitting) is of central importance to the laboratory frame double resonance experiment. The interaction, predominantly dipolar, between the protons and nitrogens causes a mixing of states in the composite system, making it possible for fluctuating fields in the crystal to induce mutual spin flip transitions. Because these transitions conserve energy they might be expected to have a rate comparable to the proton and nitrogen T_2's. Unfortunately cross-relaxation rates cannot be conveniently measured with our apparatus so it can only be assumed that because the experiment works
reproducibly the rate is fast compared with the time available for level crossing. Assuming that mutual flips can occur when the nitrogen energy splitting is within a proton linewidth (∼100 kHz) of the Larmor frequency and estimating the rate of field change in the region of level crossing to be $10^{-4} - 10^{-4}$ sec/gauss, the period available for cross-relaxation is of order $10^{-3}$ sec. Since, neglecting $T_1$ relaxation, proton magnetization appears to be independent of the rate the sample is moved between the positions (determined by the air pressure), the cross-relaxation must reach equilibrium in less than $10^{-3}$ sec.

Before an attempt is undertaken to put the level crossing process on a more quantitative basis, several simplifying assumptions have to be made. Each level crossing shall be assumed to involve only one proton and one nitrogen and the duration of cross-relaxation will be long enough for the two spin systems to reach equilibrium. The change in magnetic field from 7 kilogauss to zero is assumed to cause three distinct level crossings at three different times. In a powder sample the nitrogen energy level splittings in each crystallite depend on the angle between the principal axes of the electric field gradient and the magnetic field. Although this means neighbouring crystallites with different orientations will level cross at different fields, it shall be assumed that the level crossings in all crystallites occur at effectively the same time. This should be a valid assumption since experiments on mixtures of dissimilar crystals have indicated that there is no communication
between crystallites. Furthermore, because the proton energy energy splittings are broad (≈100 kHz linewidth), for fields smaller than about a kilogauss the level crossings are truly coincident.

If $P^+$ and $P^-$ are the populations of the upper and lower proton energy levels and $N^+$ and $N^-$ those of the two nitrogen levels involved in a level crossing and unprimed and primed variables apply before and after level crossing respectively, the following four conditions can be applied to the level crossing process.

\[
\begin{align*}
  P' + P' &= P^+ + P^- = P^+ + P^- \\
  N' + N' &= N^+ + N^- = N^+ + N^- \quad \text{conservation of particles.}
\end{align*}
\]

\[
\begin{align*}
  P^+ - P^- + N^+ - N^- &= P^+ - P^- + N^+ - N^- \quad \text{conservation of energy.}
\end{align*}
\]

\[
\begin{align*}
  P^+ &= N^+ \quad \text{equal spin temperature after level crossing.}
\end{align*}
\]

With some algebraic manipulation, these relations may be arranged to give the populations after level crossing in terms of those before level crossing.

\[
\begin{align*}
  P^+ &= \frac{P (P^+ + N^+)}{(P + N^+ + N^-)} \\
  P^- &= \frac{P (P^- + N^-)}{(P + N^+ + N^-)} \\
  N^+ &= \frac{(N^+ + N^-)(P^+ + N^+)}{(P + N^+ + N^-)} \\
  N^- &= \frac{(N^+ + N^-)(P^- + N^-)}{(P + N^+ + N^-)}
\end{align*}
\]

To simulate the sequence of the laboratory frame double resonance experiment, these equations must be applied successively to the three nitrogen energy splittings from the largest to the smallest, then the populations adjusted to account for proton relaxation and nitrogen relaxation in position 2 and for the return to position 1 the equations have to be applied three more times, on this occasion from the smallest to the largest nitrogen splitting. After only
two level crossings the equations become extremely unwieldy; the task of carrying out the entire calculation algebraically would be practically insurmountable. The solution was to use a computer. Applying these relations directly to our computer using realistic values for proton and nitrogen populations led to difficulty since, due to the short length of the computer word, the population differences showed up only in the last decimal place of the populations. Then the computer round-off errors made it impossible to obtain accurate results. This problem was overcome by re-expressing the relations in terms of a new set of variables, the population difference in the proton levels $D_p$ and those of the nitrogen levels $D_1$, $D_2$, $D_3$, and the ratio of the number of protons to the number of nitrogens $R$. For the largest level crossing:

$$D_p' = \frac{RD_p + D_1}{R + \frac{1}{3}(2 + D_2 + D_3)} \quad D_1' = \frac{\frac{1}{3}(2 + D_2 + D_3)(RD_p + L_1)}{R + \frac{1}{3}(2 + L_2 + L_3)}$$

$$D_2' = \frac{1}{2}(L_2 - D_3 - D_1) \quad D_3' = -D_2' - D_1'$$

If $N_A$, $N_B$, and $N_0$ are the populations of the three nitrogen energy levels and $N_A + N_B + N_0 = N$ the new variables are:

$$D_p = \frac{P_+ - P_-}{P} \quad D_1 = \frac{N_0 - N_A}{N} \quad D_2 = \frac{N_A - N_B}{N} \quad D_3 = \frac{N_B - N_0}{N} \quad R = \frac{1}{N}.$$  

Similar relations may be found for the other two level crossings by cyclically permuting the variables.

The level crossing equations were applied in sequence to the computer in order to obtain a better understanding of the laboratory frame double resonance experiment. An important result of this investigation was the observation that the maximum amount of proton magnetization which can be
destroyed by the nitrogens during the level crossings on the return to the high field is independent of the amount of proton magnetization remaining in the sample at the end of the uptime. Any net proton population difference remaining at the end of the uptime can only add a constant to the final proton signal. In figure V.1, the maximum amount of final proton signal which can be affected by nitrogen irradiation during the uptime is plotted as a function of the ratio of protons to nitrogens. Experimentally this should represent the measured proton signal obtained if during the uptime the proton magnetization decays to zero and the nitrogen populations remain unchanged. Figure V.1 also displays the final proton signals obtained when varying percentages of proton alignment decay during the uptime.

To compare the predictions of the simple level crossing model with experiment, the following measurements were made on a variety of samples with different values of R. First, a conventional double resonance cycle was carried out except that the proton alignment was destroyed by zero field NMR during the uptime. The final proton magnetization obtained was corrected for nitrogen relaxation during the uptime and proton remagnetization occurring on the return of the sample to position 1. Then the final proton magnetization was measured for a cycle of the same length but where the sample spent all its time in position 1. The ratio of these two quantities should fit on the lower curve in figure V.1 if the assumptions of the level crossing model are valid. Of all the compounds used, only one, pyrrole, gave a measurement which fitted on the curve - the others were above the
Figure V.1. Proton magnetization after realignment by the unirradiated nitrogens. It is expressed as a fraction of the initial proton alignment.
So it would appear that for most compounds the laboratory frame double resonance experiment is more sensitive to quadrupole resonance than the simple level-crossing model predicts. One explanation for this discrepancy is the possibility of processes, occurring at one-half the field of a single level crossing, in which two protons undergo a mutual transition with one nitrogen nucleus. Although these double level crossings would be less probable than single level crossings, they would enable the nitrogens to affect many more protons. For one compound, acetamide, the computer calculations were carried out permitting both single and double level crossings and it was predicted that the sensitivity should be eight times as great as for single level crossing alone. So it would appear that even if double level crossings had a low probability they could cause a considerable increase in sensitivity.

In figure V.2 the percentage of accessible proton magnetization (i.e. the bottom curve of figure V.1) which can be destroyed by saturation irradiation at each of the nitrogen transitions is plotted as a function of the ratio of protons to nitrogens. It is interesting that throughout the range a $\nu^+$ irradiation is capable of destroying practically all the accessible proton signal. For compounds with well separated levels these predictions are supported by experiment in that, ordinarily, $\nu^+$'s are always the strongest lines and $\nu^-$ the weakest but $\nu^-$ is usually weaker than expected.

It is possible to see intuitively why the laboratory frame
Figure V.2. Percentage of useful proton alignment which can be destroyed by saturation irradiation on each of the three quadrupole transitions.
double resonance method is less sensitive to \( V \)- than the other two transitions. In the return to the high field after either \( V^+ \) or \( V^0 \) irradiations during the uptime the protons lose alignment in all three level crossings but after \( V^- \) absorptions the protons gain alignment on the first level crossing and lose alignment on the other two level crossings.

The full and dashed lines in figures V.1 and V.2 apply to the cases where the nitrogen \( T_1 \)'s in high field are long or short compared with the downtime. In the former case the nitrogen alignment was determined by the previous level crossing with the protons and in the latter case the alignment of acetamide nitrogens in equilibrium with the high field at 77K was used. It is comforting that for a proton to nitrogen ratio greater than 2 or 3 the sensitivity of the experiment to quadrupole resonance is effectively independent of the nitrogen high field relaxation. However, as noted previously, if the nitrogens relax during the uptime the sensitivity is reduced accordingly.

Two similar calculations on the sensitivity of the laboratory frame double resonance method with a single level crossing model have been found in the literature (23, 26). In both of these treatments the approximation was made that the number of protons is much greater than the number of nitrogens in the sample. It turns out, from our data, that this approximation is valid only for ratios greater than about 3 or 4. Blinc (26) has claimed that the sensitivity of the experiment is nearly independent of the proton relaxation in zero field. This work predicts that the sensitivity
is rigorously independent of the proton zero field relaxation.

In the preceding calculations each level crossing was assumed to occur independently. If the proton energy levels were very narrow this would always be the case; however, from the short values of proton $T_2$ the proton energy levels should have linewidths of order 100 KHz. Furthermore, at low fields where the dipolar components of the proton Hamiltonian are greater than, or comparable to, the Zeeman components there is an even wider distribution of proton energies. In figures V.3 and V.4 the low frequency NMR of the protons in L-serine at several magnetic fields and two r.f. powers is illustrated. The subsidiary lines which appear when a field is applied correspond to transitions involving a net flip of two or more protons. The details of the theory of low field NMR have been covered by several authors (27, 28) and shall not be discussed here.

If the energy difference between two nitrogen quadrupole levels is less than the width of the proton energy levels, the two quadrupole levels concerned can undergo a coincident level crossing with the third level resulting in equal population differences for two of the three transitions. Then, since the probabilities for the three transitions are equal, these two transitions will have equal intensity. This happens in nitrogen containing compounds with nitrogen field gradients having $\eta$ near 0 or 1. For $\eta$ near 1 the $V_-$ and $V_0$ transitions level cross together and it is found experimentally that $V_-$ and $V_0$ are approximately equal and relatively weak in intensity while $V_+$ lines are stronger.
Figure 1. 3. Low frequency proton absorption in L-serine at low power (~50 milligauss).
Figure IV.4: Low frequency proton absorption in L-serine at high power (~1 gauss).
This behaviour can be predicted from the single level crossing model if the simultaneous level crossings are accounted for (29).

A different situation arises in compounds where $\eta$ is near zero since in zero field the protons can have energy splittings of the same order as the $\nu_0$ transition energy. Then the nitrogens undergo continuous $\nu_0$ cross-relaxation with the protons and the population difference in the protons of this energy splitting is reflected in the difference in intensity between the $\nu^+$ and $\nu^-$ quadrupole transitions. If the proton population difference is large the A quadrupole level of the nitrogens will have a correspondingly smaller population than the B quadrupole level so that $\nu^+$ is stronger than $\nu^-$. On the other hand, if there is no proton alignment the A and B quadrupole levels should have equal populations and $\nu^+$ and $\nu^-$ should have the same intensity.

It is ordinarily impossible to detect $\nu_0$ in these circumstances; even if there is a population difference between the A and B quadrupole levels direct absorption by the protons obscures the quadrupole spectrum.

The idea that the nitrogens and protons are in continuous thermal contact in samples with low $T_1$'s has been proven experimentally. If the zero field $T_1$ of the protons is comparable to the duration of the uptime the degree of alignment of the protons can be changed by varying the length of the uptime. For short uptimes the protons retain most of their alignment and $\nu^+$ is found to be stronger than $\nu^-$ but for long uptimes the protons lose most of their magnetization and $\nu^+$ and $\nu^-$ are found to be equal in intensity. If $\eta$
a high power low frequency field ($\sim 50$ kHz) is applied to the protons their alignment is destroyed even during a short uptime and then $V^+$ and $V^-$ are equal. If a suitably large d c magnetic field is imposed on the sample curing the uptime the $V$ level crossing can be prevented. In this case the intensity of $V^+$ and $V^-$ transitions is independent of the duration of the irradiation period indicating no cross-relaxation can take place.

If a compound has a nitrogen $V$ of order 200 kHz or more it is possible to artificially produce continuous thermal contact between two of the nitrogen levels and the protons by applying at position 2 a magnetic field large enough to match the proton levels to $V$. This can give increased sensitivity to $V^-$ transitions as demonstrated in figure V.5. If a field which gives the protons a Larmour frequency equal to one-half the nitrogen $V$ is applied to the sample during the uptime the $V^-$ intensity can be enhanced to a degree dependent on the proton alignment. This is evidence for the existence of cross relaxation processes involving two protons and one nitrogen nucleus. As mentioned before, even a low probability double level crossing process could account for the discrepancy between the experimental sensitivity of the apparatus and that predicted from a single level crossing model.

Deuterium quadrupole resonance frequencies occur in the range from 90 to 200 kHz. This is within the proton energy distribution in zero field so there is continuous cross-relaxation between the deuterons and the protons and the
Figure IV.5. Effect of the application of a magnetic field on $V_-$ intensity in DL-glutamic acid hydrate ($v_0=150$ kHz).
simple level crossing model used previously for nitrogen is not applicable. In the case of nitrogens with $\eta$ near zero thermal contact with the protons was through the $\nu_0$ transition but for deuterons all three transitions may cross-relax with the protons. This means that if the protons lose alignment in zero field the deuterons tend to relax as well and the sensitivity of the experiment drops. Hence it is advantageous to do deuterium quadrupole resonance with short uptimes if the proton zero field $T_1$ is short.

Because the low field NMR spectrum of the protons overlaps the deuterium spectrum, the power of irradiation in deuterium resonance must be low to prevent direct proton absorption from obscuring the deuterium lines. Even relatively small DC magnetic fields (~10g) can ruin a deuterium spectrum since the deuterons have a larger magnetic moment than nitrogens and are in general much less quenched by their quadrupole interaction.

The intensities of the $\nu^+$ and $\nu^-$ lines in deuterium spectra do not differ as much as in a nitrogen spectrum. $\nu^+$ and $\nu^-$ are generally about equal but lines at frequencies lower than about 110 kHz and also those at frequencies higher than about 180 kHz tend not to be so intense as those in the intermediate region. The decline in sensitivity in the upper frequency region might be due to the drop in the number of protons of high energies. In the zero field NMR spectrum of protons there is a sharp drop in absorption above 160 kHz. Deuterium $T_1$'s are never observed.

Although the details of the processes involved in the
laboratory frame double resonance technique are very complex, the basic reasons for the high sensitivity of the method are quite simple. The intensity of a quadrupole resonance line, as measured by most techniques, is proportional to the population difference between the two levels concerned. In zero magnetic field the equilibrium population differences of nitrogens and deuterons are not very large because the quadrupole splittings are small. Since both nuclei have small magnetic moments, large fields are required to produce a reasonable energy splitting. But in laboratory frame double resonance the population difference in the quadrupolar nuclei is determined by the high field proton alignment which is not only large but also independent of the quadrupole frequency region being examined. Whereas for most NQR techniques the sensitivity of the detection is poorer at lower frequencies, in the laboratory frame double resonance method all the detection is carried out at one frequency - the proton Larmor frequency in the high field. In fact laboratory frame double resonance NQR is comparable to doing CW NQR at a constant frequency of 30 MHz.
Chapter VI. Some Background Topics.

As explained earlier, a sample is amenable to NQR by the laboratory frame double resonance method only if its proton $T_1$ is in the range 5 sec - several minutes; so it is of some interest to know the origins of proton spin-lattice relaxation. The two dominating causes of $T_1$ relaxation of protons in the samples used in this research are a) the presence of paramagnetic impurities and b) the occurrence of motion in molecular groups.

There are many references (e.g. 30, 33) on proton relaxation by paramagnetic impurities so it will be discussed only very briefly here. Protons with an unpaired electron nearby can undergo mutual transitions induced by the magnetic dipolar interaction. This interaction affects only those protons within the sphere of influence of a paramagnetic site and the subsequent equilibrating of proton spin temperature throughout the sample is achieved through the slower process of spin diffusion by proton spin-spin interactions.

The proton $T_1$ due to paramagnetic impurities is normally inversely proportional to the number of impurity sites (30) but when the concentration of paramagnetic ions exceeds about 1%, every proton is within the sphere of influence of an unpaired electron so spin diffusion is unnecessary and the $T_1$ is independent of concentration. In dilute samples the $T_1$ becomes slightly shorter as the temperature is raised while in more concentrated samples it is independent of temperature. The proton $T_1$ in samples containing paramagnetic sites usually increases as the magnetic field increases.
VI.2

In many organic compounds there exist molecular groups which can reorientate about a particular bond direction. For example, often in methyl groups where the hydrogens are only weakly held in position by intermolecular forces there is a low barrier to rotation of the group about the bond between the carbon atom and the rest of the molecule. Even in the \( N^+H_3 \) radicals of amino acids where the hydrogen atoms are involved in hydrogen bonds, rotation can occur about the C-N bonds. The motion of a methyl or a \( N^+H_3 \) group is not actually a rotation but rather a random process of reorientation of the hydrogen atoms between the three equilibrium positions of the group. The extent of the reorientation motion is determined by the potential barrier \( V \) between equilibrium positions. A number of groups proportional to \( \exp(-V/kT) \) will have enough energy to move from one position to another. Because the local fields at each position are different, as a particular proton moves from position to position it is subjected to a fluctuating field. Components of this field at the Larmour frequency of the proton will induce transitions and hence provide a means of spin-lattice relaxation.

For times smaller than the correlation time \( \gamma_c \), the state of a particular proton may be considered unchanged but for longer times it will have undergone reorientation to another position. Since for higher temperatures the number of groups capable of overcoming the barrier to reorientation is larger, this correlation time becomes shorter as the temperature increases. For a particular value of \( \gamma_c \), the spectral density imposed on a proton is found to be approximately
constant for frequencies from 0 up to a cut-off frequency \( \nu_c = 1/\gamma \) (3 pg 295). Because the total integrated intensity over all frequencies is constant for all values of \( \gamma \), as \( \gamma \) becomes shorter the intensity of the component of the fluctuating field at a particular frequency \( \nu \) is first zero since \( \nu \gg \nu_c \) reaches a maximum for \( \gamma \) such that \( \nu \sim \nu_c \) and gets smaller as \( \gamma \) is shortened still further. This means that the number of transitions induced, proportional to the proton \( T_1 \), is small for long \( \gamma \), a maximum when the Larmour frequency \( \nu_L = \gamma \) and then is again small for short \( \gamma \).

Since \( \gamma \) is a decreasing function of temperature the proton \( T_1 \) should be long for low temperatures, have a minimum for the temperature at which \( \nu_L = 1/\gamma \), and then increase at higher temperatures. This is a well proven experimental fact. If a magnetic field is applied to the sample the proton Larmour frequency increases and the \( T_1 \) minimum occurs at a higher temperature.

The practical advantage of a knowledge of how \( T_1 \) varies with temperature is that if a particular sample has a proton \( T_1 \) which is too fast at nitrogen temperature it may be possible to lengthen the \( T_1 \) to an acceptable value by changing the temperature. For samples in which the dominant relaxation process is from paramagnetic impurities it may be possible to raise the \( T_1 \) to an acceptable value by operating the experiment at a lower temperature. However, in practice, this has not yet been successful. But in samples where the relaxation is from rotating molecular groups the \( T_1 \) can be lengthened considerably by operating at a temperature further from the one at which the \( T_1 \) minimum occurs.
VI.4

In proton spin-lattice relaxation the magnetic dipolar interaction with neighbouring protons or paramagnetic sites induces practically all the relaxation transitions, but in nitrogens and deuterons this interaction is reduced considerably because of the smaller magnetic moments of these nuclei. However they do possess an electric quadrupole moment which can interact with oscillating electric fields from either paramagnetic impurities or lattice vibrations and is the dominant source of $T_1$ relaxation. For nitrogens and deuterons the $T_1$'s can be expected to get shorter as the temperature is raised.

A special case occurs in samples containing deuterons or nitrogens with two closely spaced energy levels. Then, as discussed in the previous chapter, when the proton energy levels are of the same order as a quadrupole splitting, cross-relaxation processes can occur through magnetic dipolar interactions between the two species. This is especially important in deuterium where the energy splittings are never very different from those of the protons. If the coupling between the deuterons and protons is strong the $T_1$'s of the two species will be similar.

The study of the temperature dependence of nitrogen and deuterium NQR lines has not played a large role in the research for this thesis, however, it is important to ascertain that differences in NQR frequencies are due to differences in electric field gradients rather than a result of varying motional averaging.

It is well known (16 page 40) that the torsional motions
of molecules in crystals are at much higher frequencies than the quadrupole frequencies so the nucleus sees a net temperature-dependent averaged field gradient which is different from what it would see if the molecule were stationary. The result of this field gradient tensor averaging is to cause the measured NQR frequencies to decrease as the temperature increases and the torsional oscillation amplitudes increase. This effect can be quite extreme when the sample is at a temperature near a phase transition. There are several references on the temperature dependence of NQR frequencies (31).

In pyrazine the $e^2qQ$ of the nitrogen decreased by 10 kHz between 4.2K and 77K and $\eta$ increased by less than 5% (32). The $e^2qQ$ and $\eta$ of L-serine hydrate were found with our apparatus to have decreased by 5 kHz and 1% between 20K and 77K. On this basis, it will be assumed when considering nitrogen NQR frequencies in molecular crystals at 77K, to a good approximation motional averaging effects can be neglected.

The temperature dependence of the deuterium $e^2qQ$ in deuterated chloroform was found to be 0.02 KHz per degree at 100K (33). With our apparatus the amino acid OD deuteron $e^2qQ$ in L-serine monohydrate was found to change less than one KHz between 20K and 77K. With this evidence it has been assumed that at 77K motional averaging effects can be neglected for deuterium as well as nitrogen.

Contrary to what the simple motional averaging theory predicts it has been found in several samples that the nitrogen and deuterium $e^2qQ$'s at room temperature were larger
VI.6

than at 77K. The logical explanation is that the anomalous change in $e^2qQ$ is due to a change in the crystal structure which occurs as the sample is heated.

There are two fundamental causes of quadrupole line broadening in the samples used in this research; homogeneous broadening, which results from an intrinsic broadening of the spin levels and inhomogeneous broadening caused by the presence of a distribution of transition frequencies. Two common causes of homogeneous broadening are spin-spin interactions and interaction with the r.f. field, while crystal lattice irregularities, unresolved fine structure and dipolar interaction with dissimilar neighbouring spins can give rise to inhomogeneous broadening.

Experimentally a relatively wide range of linewidths of nitrogen quadrupole lines is found. The narrowest are 2-4 KHz (full width at half height) and from this there is a continuous range up to 50 KHz or more. There is a much smaller distribution of deuterium linewidths; OD widths lie in the approximate range 0.6 to 0.8 KHz and ND widths in the region from about 1 to 1.3 KHz, however larger widths may be observed in the presence of unresolved fine structure (see chapter VIII) or in partially deuterated OD 's or ND 's (see chapter IX). The difference between CD and ND linewidths may be a consequence of the shorter distance and greater strength of the OD bond. For both nitrogen and deuterium these widths increase as the r.f. power is increased.
Chapter VII. Solid Effect Transitions in Nitrogen Quadrupole Resonance.

Since in most of the compounds in which nitrogen $^{14}$ NQR can be carried out with the laboratory frame double resonance method the nitrogen atom is covalently bonded to one or more protons, some understanding of the composite nitrogen-proton system is necessary to account for the shape of the double resonance spectra.

Two types of interaction can occur between a nitrogen nucleus and a proton: a direct coupling of the dipolar moments of the two nuclei through the magnetic dipolar interaction and an indirect coupling of the two nuclei by way of the electrons in the bond joining them. The direct dipolar interaction, calculated with the familiar formula, is typically of the order of a few kilocycles. The indirect nitrogen-proton interaction is proportional to the product of four quantities: the gyromagnetic ratios of each nucleus and the hyperfine interaction constants for the $S$ electrons for each atom (16pg 30). Because the hydrogen atom has a small hyperfine interaction, the indirect spin-spin coupling is small for the $^{14}_N-H$ system. In fact the indirect $^{14}_N-H$ scalar spin-spin coupling has been measured in several compounds and has been found to be less than a tenth of a kilocycle (34). Then, the dominant nitrogen-proton interaction is taken to be the direct magnetic dipolar interaction.

The general system of a nitrogen nucleus and one directly bonded proton in a magnetic field will now be considered. The Hamiltonian is made up essentially of the following terms:
\[ \mathcal{H} = \mathcal{H}_{\text{quadrupole}} + \mathcal{H}_{\text{Zeeman nitrogen}} + \mathcal{H}_{\text{Zeeman proton}} + \mathcal{H}_{\text{dipolar nitrogen-proton}} \]

It will be assumed that all the quadrupole frequencies are large compared with the linewidth of the proton energy levels. For all but the highest magnetic fields \( \mathcal{H}_{\text{quadrupole}} \) will be the largest term in the total Hamiltonian. Because the proton gyromagnetic ratio is an order of magnitude greater than the nitrogen gyromagnetic ratio the proton Zeeman operator contributes larger matrix elements than the nitrogen Zeeman operator. It is convenient to use product wave functions of the form \( \psi_n \psi_p \) where \( \psi_n \) denotes the eigenvectors of a spin 1 system in zero magnetic field and \( \psi_p \) the proton magnetic base states \( |\frac{1}{2}\rangle, |\frac{1}{2}\rangle \). Using the principal axes of the electric field gradient tensor as the axes of quantization, the Hamiltonian has been calculated and is shown in figure VII.1.

The energy levels and allowed transitions of the nitrogen-proton system shall be considered in three stages: 1) no applied magnetic field and no interaction between the two nuclei, 2) an applied magnetic field but no interaction between the two nuclei and 3) an applied magnetic field with an interaction between the two nuclei.

The first case is very simple. There are three sets of doubly degenerate levels whose energy spacing is determined entirely by the quadrupole Hamiltonian. As shown in Chapter II the introduction of an r.f. field can induce three transitions at the quadrupole frequencies \( \nu_+ \), \( \nu_- \) and \( \nu_0 \).

When a magnetic field is applied the degeneracies are removed by the proton Zeeman Hamiltonian. If the nitrogen
<table>
<thead>
<tr>
<th></th>
<th>( A_1, 1/2 )</th>
<th>( A_1, -1/2 )</th>
<th>( B_1, 1/2 )</th>
<th>( B_1, -1/2 )</th>
<th>( 10, 1/2 )</th>
<th>( 10, -1/2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1, 1/2 )</td>
<td>( (1 + \eta) ) Q</td>
<td>-( 1/2 ) ( Y_P ) ( H ) ( \sin \beta ) ( e^{-i\psi} )</td>
<td>-( 3/2 ) ( D ) ( \sin \alpha ) ( \cos \theta )</td>
<td>-( 1/2 ) ( D ) ( \sin \alpha ) ( \cos \beta )</td>
<td>-( 3/2 ) ( D ) ( \sin \alpha ) ( \cos \eta )</td>
<td>-( 3/2 ) ( D ) ( \sin \alpha ) ( \cos \theta )</td>
</tr>
<tr>
<td>( A_1, -1/2 )</td>
<td>-( 1/2 ) ( Y_P ) ( H ) ( \sin \beta ) ( e^{-i\psi} )</td>
<td>(1 + ( \eta )) Q</td>
<td>-( 1/2 ) ( D ) ( \sin \alpha ) ( \sin \beta ) ( e^{-i\psi} ) +( 1/2 ) ( D ) ( \sin \alpha ) ( \cos \theta )</td>
<td>-( 1/2 ) ( Y_P ) ( H ) ( \cos \beta )</td>
<td>-( 3/2 ) ( D ) ( \sin \alpha ) ( \cos \eta ) ( \cos \beta )</td>
<td>-( 1/2 ) ( Y_P ) ( H ) ( \sin \beta ) ( \cos \beta )</td>
</tr>
<tr>
<td>( B_1, 1/2 )</td>
<td>-( 1/2 ) ( D ) ( \sin \alpha ) ( \cos \theta )</td>
<td>-( 3/2 ) ( D ) ( \sin \alpha ) ( \cos \theta ) ( e^{-i\psi} )</td>
<td>(1 - ( \eta )) Q</td>
<td>-( 1/2 ) ( Y_P ) ( H ) ( \sin \beta ) ( e^{-i\psi} )</td>
<td>-( 3/2 ) ( D ) ( \sin \alpha ) ( \sin \beta ) ( \cos \eta )</td>
<td>-( 3/2 ) ( D ) ( \sin \alpha ) ( \cos \theta ) ( \cos \beta )</td>
</tr>
<tr>
<td>( B_1, -1/2 )</td>
<td>-( 3/2 ) ( D ) ( \sin \alpha ) ( \sin \beta ) ( e^{-i\psi} ) +( 3/2 ) ( D ) ( \sin \alpha ) ( \cos \theta ) ( e^{-i\psi} )</td>
<td>-( 1/2 ) ( Y_P ) ( H ) ( \cos \beta )</td>
<td>-( 1/2 ) ( Y_P ) ( H ) ( \sin \beta ) ( e^{-i\psi} )</td>
<td>(1 - ( \eta )) Q</td>
<td>-( 1/2 ) ( Y_P ) ( H ) ( \sin \beta ) ( e^{-i\psi} )</td>
<td>-( 1/2 ) ( Y_P ) ( H ) ( \sin \beta ) ( e^{-i\psi} )</td>
</tr>
<tr>
<td>( 0, 1/2 )</td>
<td>-( 3/2 ) ( D ) ( \sin \alpha ) ( \cos \theta )</td>
<td>-( 1/2 ) ( D ) ( \sin \alpha ) ( \cos \beta ) ( e^{-i\psi} ) -( 1/2 ) ( Y_P ) ( H ) ( \cos \beta )</td>
<td>-( 3/2 ) ( D ) ( \sin \alpha ) ( \cos \eta ) ( \cos \beta ) ( e^{-i\psi} )</td>
<td>-( 1/2 ) ( Y_P ) ( H ) ( \sin \beta ) ( e^{-i\psi} )</td>
<td>-( 2 ) ( D ) ( \sin \alpha ) ( \cos \theta ) ( \cos \beta ) ( e^{-i\psi} )</td>
<td>-( 2 ) ( D ) ( \sin \alpha ) ( \cos \beta ) ( \cos \eta ) ( e^{-i\psi} )</td>
</tr>
<tr>
<td>( 0, -1/2 )</td>
<td>-( 3/2 ) ( D ) ( \sin \alpha ) ( \cos \theta ) ( e^{-i\psi} ) +( 3/2 ) ( D ) ( \sin \alpha ) ( \cos \eta ) ( \cos \beta ) ( e^{-i\psi} )</td>
<td>-( 1/2 ) ( Y_P ) ( H ) ( \cos \beta )</td>
<td>-( 1/2 ) ( Y_P ) ( H ) ( \sin \beta ) ( e^{-i\psi} )</td>
<td>-( 3/2 ) ( D ) ( \sin \alpha ) ( \cos \theta ) ( \cos \beta ) ( e^{-i\psi} )</td>
<td>-( 2 ) ( D ) ( \sin \alpha ) ( \cos \beta ) ( \cos \eta ) ( e^{-i\psi} )</td>
<td>-( 2 ) ( D ) ( \sin \alpha ) ( \cos \beta ) ( \cos \eta ) ( e^{-i\psi} )</td>
</tr>
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</table>

**Figure VII.1.** Hamiltonian of the nitrogen-proton system. The axes are taken along the principal electric field gradient axes at the nitrogen site. The nitrogen-proton direction is at angles \( \Theta, \Phi \) to the quantization axes and the external magnetic field \( H \) is at angle \( \beta, \Psi \) to the quantization axes.
Zeeman interactions are neglected, the new eigenstates with respect to the field gradient principal axes are $|A\rangle|1\rangle$, $|A\rangle|2\rangle$, $|B\rangle|1\rangle$, $|B\rangle|2\rangle$, $|1\rangle|1\rangle$, and $|1\rangle|2\rangle$ (11) and 12 denote the projections of proton states $|\frac{1}{2}\rangle$, $|\frac{-1}{2}\rangle$ along the z principal field gradient axis which diagonalize the Zeeman hamiltonian with a magnetic field applied in a general direction. If there is no nitrogen-proton coupling, an r.f. field can only induce transitions between states differing by the pure quadrupole frequencies leaving the proton states unchanged or between the Zeeman split proton states (differing by the frequency $\gamma_{pH}$) leaving the quadrupole states unaffected. It cannot induce transitions which change the states of both the nitrogen and the proton.

The effect of the magnetic dipolar interaction between the nitrogen and the proton is to cause a mixing of the states which makes previously forbidden transitions allowed. The state $|A\rangle|1\rangle$ becomes $|A\rangle|1\rangle + a|B\rangle|1\rangle + b|1\rangle|2\rangle + c|0\rangle|1\rangle + d|0\rangle|2\rangle$ neglecting terms of higher order. The mixing terms $a$ and $b$ are of order $(\frac{\gamma_{pH}^{3}}{r^{3}})^{2}$ and $c$ and $b$ are of order $(\frac{\gamma_{pH}}{r^{3}})^{2}$. The other states are changed similarly.

Now, when an r.f. field is applied there are additional allowed transitions at frequencies $\nu_{+\pm}\gamma_{pH}$, $\nu_{-\pm}\gamma_{pH}$, and $\nu_{0}\pm\gamma_{pH}$. These new transitions which shall be called proton satellites are a form of the well known solid effect (3, 35). The transition probabilities of these proton satellites vary as the inverse square of the main quadrupole line so satellite lines about $\nu_{0}$ should be more intense than those about the other two quadrupole transitions.
Then the quadrupole spectrum of a nitrogen bonded to a proton should consist not only of the three quadrupole lines $V_+$, $V_-$, and $V_0$ but also proton satellite lines located at frequencies $\gamma_p H$ each side of the main quadrupole lines. Experimentally, in an N-H compound with no applied magnetic field, as the power of the r.f. field is increased ($\geq 1$ gauss peak to peak) a broad absorption appears centred on each of the quadrupole lines. If the r.f. power is increased to a very high level this broad absorption can obscure the main quadrupole line. When a static magnetic field $H$ is applied, the absorption splits into two satellites of linewidth 20-30 KHz at frequency $\gamma_p H$ above and below the quadrupole lines.

In many of the nitrogen compounds used in this thesis, the nitrogen was bonded to two or more protons and the proton satellites were different from the N-H case. In a theoretical treatment of the case where two protons are bonded to a nitrogen a composite wave function of the form $\Psi_N \Psi_P \Psi_P$ may be used. There is one new term to be added to the Hamiltonian used earlier, the dipolar interactions between the two protons. As before, the appropriate base states for $\Psi_N$ are the pure quadrupole eigenstates $|A\rangle$, $|B\rangle$, and $|0\rangle$. For the proton states it is convenient to use those state vectors which diagonalize the Hamiltonian of the 2 proton system ($\mathcal{H}_{\text{Zeeman}} + \mathcal{H}_{\text{dipolar}}$). It would be cumbersome to write out a complete Hamiltonian for the NH$_2$ system but, briefly, it consists of a 12 x 12 matrix in which the diagonal elements are composed of the pure quadrupolar energies and the terms of the diagonalized Hamiltonian of
the two proton system. The off-diagonal elements are contributed by the nitrogen Zeeman terms and the nitrogen-proton dipolar interaction. Because the quadrupole terms are so much greater than any of the other terms it is a good approximation to neglect the off-diagonal elements when calculating the energy levels of the NH₂ system. So, the problem of finding the energy levels of the NH₂ system reduces to that of diagonalizing the two proton Hamiltonian.

In zero applied field the only interaction between the two protons is the dipolar interaction. In terms of the magnetic base states, \(|\frac{1}{2}, \frac{1}{2}\rangle, |\frac{1}{2}, -\frac{1}{2}\rangle, |\frac{1}{2}, \frac{1}{2}\rangle, |\frac{1}{2}, -\frac{1}{2}\rangle, |\frac{1}{2}, \frac{1}{2}\rangle, |\frac{1}{2}, -\frac{1}{2}\rangle\), this gives the following Hamiltonian:

\[
\mathcal{H}_0 = \begin{pmatrix}
A & -C & -C & E \\
-L & -A & B & C \\
-D & B & -A & C \\
F & L & D & A
\end{pmatrix}
\]

where A, B, ...F are the terms of the Van Vleck expansion of the dipolar operator. If the Z quantization axis is chosen along the H-n direction (i.e. \(\theta = \phi = 0\)), then

\[A = -\frac{\gamma_p^2 \hbar}{2r^3}, \quad B = \frac{\gamma_0^2 \hbar}{r^3}, \quad C = D = E = F = 0.\]

Now the Hamiltonian may be diagonalized by transforming to the triplet states \(|\frac{1}{2}, \frac{1}{2}\rangle, \sqrt{2}(|\frac{1}{2}, -\frac{1}{2}\rangle + |\frac{1}{2}, \frac{1}{2}\rangle), |\frac{1}{2}, -\frac{1}{2}\rangle\) and the singlet state\(|0\rangle(\frac{1}{2}, \frac{1}{2} - |\frac{1}{2}, -\frac{1}{2}\rangle, |\frac{1}{2}, \frac{1}{2}\rangle\). Then the Hamiltonian becomes:

\[
\mathcal{H}_0 = \gamma_p^2 \hbar \frac{r}{r^3} \begin{pmatrix}
\frac{1}{2} & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & -\frac{1}{2} & 0 \\
0 & 0 & 0 & 0
\end{pmatrix}
\]

a small r.f. field can only induce transitions of frequency \(\frac{\gamma_p^2 \hbar}{2r^3}\) between triplet states. Then in zero applied field the proton satellites of an NH₂ system will be displaced from the main quadrupole by the frequency \(\frac{3}{2} \gamma_p^2 \hbar \frac{r}{r^3}\). This is
observed experimentally and it can be used to estimate the separation between the two protons in an \( \text{NH} \) group. For acetamide and L-proline the H-H distances were predicted 1.9 and 1.5 angstroms respectively. The neutron diffraction structures of these compounds are not yet known but these distances are consistent with those predicted from H\( \text{N} \)H \( \text{H} \) angles of 120° and 109.5° and N-H distances of 1 angstrom.

When a magnetic field is applied to an \( \text{NH}_2 \) group such that \( \gamma_{\text{pH}} \) is much greater than \( \frac{\gamma_{\text{pH}}^2}{r^3} \) the energy of the two proton system is determined by the Zeeman interaction. The resulting Hamiltonian using magnetic base states quantized along the magnetic field is:

\[
\mathbf{H} = \gamma_{\text{pH}} \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & -1
\end{pmatrix}
\]

If an r.f. field is applied at 90° to \( \text{H} \) there should be two transitions, one at frequency \( \gamma_{\text{pH}} \) and the other at frequency \( 2\gamma_{\text{pH}} \) (the second transition can only occur when there is an interaction linking the \( |\frac{1}{2}, \frac{1}{2}\rangle \) and \( |\frac{1}{2}, -\frac{1}{2}\rangle \) states). It follows that in \( \text{NH}_2 \) groups, proton satellites should be observable at frequencies \( \gamma_{\text{pH}} \) and \( 2\gamma_{\text{pH}} \) from the main quadrupole lines. In figure VII.2, the proton satellites on the \( V^+ \) line of acetamide are shown for three values of the applied magnetic field.

Although it is not difficult to solve the two proton Hamiltonian when the magnetic field is zero or very large, in the intermediate region where the proton Zeeman and dipolar energies are of the same order the problem increases in complexity. If the H-H direction is at angle \( \Theta, \phi \) to the
Figure XII. 2. Field dependence of the proton satellites on the acetamide $V_1$ line. The much weaker satellites at frequency $V_1 + 2V_p H$ are not shown.
magnetic field, the two proton Hamiltonian becomes, in
terms of the triplet and singlet states, quantized along
the magnetic field

\[ \mathcal{H} = D \begin{pmatrix}
    h' + A & -\sqrt{2}C & -E & 0 \\
    -\sqrt{2}C^* & -2A & \sqrt{2}C & 0 \\
    -E^* & \sqrt{2}C^* & -h' + A & 0 \\
    0 & 0 & 0 & 0
\end{pmatrix} \]

where \( h' = 2p^2h/(\hbar^2r^3) \) \( A = \frac{1}{4} (1 - 3 \cos^2 \phi) \), \( C = \frac{3}{4} \sin \phi \cos \phi \ e^{-i \phi} \)

\[ D = \frac{\gamma_p \hbar}{r^3} \]

This leads to the secular equation:

\[ -\lambda^3 + \lambda \left[ 3\lambda^2 - 4|c|^2 + h'^2 + |e|^2 \right] + 2A h' = 2A^3 - 4|c|^2 + 4|c|^2|e| + 2A|e|^2 = 0 \]

If \( \cos \phi \) is represented by \( X \) this reduces to the simple
equation

\[ -\lambda^3 + \lambda \left( \frac{X}{4} + H'^2 \right) + \frac{1}{4} + \frac{1}{2} \left( 3x^2 - 1 \right) H'^2 = 0 \]

The eigenvectors corresponding to each eigenvalue are ob­tained from the cofactors of the above matrix

\[ \psi = \begin{pmatrix} a e^{i \phi} \\ b \\ c e^{-i \phi} \end{pmatrix} \]

where, before normalization,

\[ a = \lambda^2 + \lambda (A + h') - 2A^2 + 2AH' - 2|c|^2 \]
\[ = \lambda + \frac{A}{4} (1 - 3x^2 + 4H') + \frac{1}{2} (1 - 3x^2) h' - \frac{1}{8} (3x^2 - 1) \]
\[ b = -\frac{3\sqrt{2}}{4} X (1 - 3x^2)^{1/2} (H' + h) \]
\[ c = -3/8 (1 - x^2) (1 - 2 \lambda) \]

Now if an r.f. field is applied at 90° to the static field
(x direction) the transition probability of a particular
transition from \( \lambda \) to \( \lambda' \) will be proportional to:

\[ \left| \left( a e^{-i \phi} \langle \frac{1}{2}, \frac{1}{2} | + b e^{-i \phi} \langle \frac{1}{2}, -\frac{1}{2} | + c e^{-i \phi} \langle -\frac{1}{2}, \frac{1}{2} | + d e^{-i \phi} \langle -\frac{1}{2}, -\frac{1}{2} | \right) I_x \right( a e^{i \phi} | \frac{1}{2}, \frac{1}{2} > + b e^{i \phi} | \frac{1}{2}, -\frac{1}{2} > + c e^{i \phi} | -\frac{1}{2}, \frac{1}{2} > + d e^{i \phi} | -\frac{1}{2}, -\frac{1}{2} > \right| \]

\[ = \frac{1}{2} \left| \left( a' b' + b' c' \right) e^{i \phi} + (a' b + c b') e^{-i \phi} \right|^2 \]
where the primed and unprimed eigenvectors represent $\lambda'$ and $\lambda$ respectively.

The calculation above yields the frequencies and relative transition probabilities of the three transitions in an H-H group when the H-H direction is at angles $\Theta$, $\phi$ to the applied magnetic field. Since the usual experimental situation is a powder it is necessary to add up the contributions from crystallites at all values of $\Theta$ and $\phi$. The obvious way to carry out this angular average is to use a computer. The procedure used was to divide the entire frequency range into small intervals, the aim being to produce a frequency distribution function which would represent the probability of a transition within each of the frequency ranges. The transition frequencies depend only on $\Theta$ so that all transitions are accounted for if the secular equation is solved for the range $\Theta = 0$ to $\Theta = 180$. The difference in solid angle at different values of $\Theta$ was taken care of by stepping in fixed increments of $\cos \Theta$ rather than $\Theta$. The transition probability was calculated for each value of $\cos \Theta$ and averaged over $\phi$ using the property $\langle \cos^2 \phi \rangle = \langle \sin^2 \phi \rangle = \frac{1}{2}$ over a cycle. For each transition, the transition probability was stored in the element corresponding to the appropriate frequency range in the array of the function representing the frequency distribution.

The results of this calculation are shown in figure VII.3 where the mean frequency of the proton satellite for each
Figure VII.3. The frequency separation between the acetamide $\nu_0$ and its upper satellite as a function of applied field. The smooth curve represents the theoretical separation.
value of $H$ is plotted along with experimental data taken from the proton satellites on the $V_+^+$ of acetamide. Unfortunately the experimental error is too large to permit a fair comparison between theory and experiment.

In many of the nitrogen sites studied in this thesis the nitrogen atom was bonded to three hydrogen atoms. This is a more difficult system to examine theoretically and the experimental data on $NH_3$ satellites is not yet good enough to allow quantitative comparison between theory and experiment. In zero applied magnetic field the proton satellites on an $NH_3$ group cover a wide range of absorption which begins at a frequency well below and ends an equal distance above the main quadrupole line. When the applied field is large there are strong proton satellites at frequencies $\nu_N \pm \nu_p H$ and weaker ones at $\nu_N \pm 2\nu_p H$. Tony White, a colleague in our research group, is currently carrying out a theoretical and experimental study of $NH_3$ satellites.

Contrary to what one might expect, proton satellites have been observed on lines belonging to nitrogens which have no direct bonds with hydrogen atoms. One example is imidazole where satellites have been measured on both sets of quadrupole lines. In imidazole $\text{NH}_2\text{CH}:\text{N.C}.\text{H}:\text{CH}$ it turns out, from the crystal structure, that the nitrogen with no covalent bonds with protons takes part in a hydrogen bond.

To a limited extent proton satellites may be used in the assignment of nitrogen lines. When a magnetic field is
applied, the satellite spectrum of all nitrogen sites are essentially the same regardless of how many protons are directly bonded to the nitrogen, the only notable difference being that \( \text{NH}_2 \) and \( \text{NH}_3 \) groups often have weak satellites at \( 2\gamma \text{pH} \) from the quadrupole line. However in zero field the situation is somewhat better: \( \text{N}'s \) and \( \text{N}-\text{H}'s \) have satellites centred on the quadrupole line, \( \text{NH}_2 \)'s have satellites at frequencies \( \frac{3\nu + \frac{1}{2}}{2} \) on either side of the quadrupole line and \( \text{NH}_3 \)'s have a very broad absorption centred on the quadrupole line. Unfortunately since satellites are usually broad (20-30 kHz) and sometimes rather weak it is often very difficult to distinguish the different types so considerable caution must be exercised when using this method to assign nitrogen lines.

The intensity of a magnetic resonance absorption is proportional to the population differences between the two levels of the system undergoing the transition. In the composite nitrogen proton system an upper proton satellite on a particular quadrupole line involves the levels \( \Lambda + \Lambda' + P + P' \) and \( \Lambda - \Lambda' - P - P' \) and a lower satellite involves the levels \( \Lambda + \Lambda' + P - P' \) and \( \Lambda - \Lambda' - P + P' \) where \( \Lambda, \Lambda', P, P' \) denote the populations of the upper and lower nitrogen and proton energy levels. If the proton zero field \( T_1 \) is long compared with the uptime the population \( P' \) will be greater than \( P \) and similarly \( \Lambda' \) will be greater than \( \Lambda \) if the nitrogen zero field \( T_1 \) is long. Then for an upper proton satellite both the nitrogen and proton alignments are in the same direction, but for a lower
satellite the alignments are in the opposite directions. Then in the composite system the net population difference is much greater for upper satellites than for lower satellites and if the transition probabilities for the two transitions are equal (supported by experiment) the upper satellite should be more intense than the lower satellite.

The laboratory frame double resonance technique measures the proton magnetization at the end of the experimental cycle. In Chapter V it was found that the depth of absorption obtained for a pure nitrogen quadrupole line is independent of the alignment of the protons remaining at the end of the uptime. But, since satellite transitions directly change the proton alignment, if the proton zero field $T_1$ is long enough, the measured signal can be affected by proton alignment changes during the uptime. In upper satellites the net effect is a reduction in proton magnetization and in lower satellites an increase in proton magnetization.

In a sample where the proton zero field $T_1$ is comparable to the uptime it should be possible to test these predictions. If the uptime is made very short then any information contained in the proton alignment will be retained and the upper satellite should be larger than the lower one. If, on the other hand, the uptime is made very long compared with the zero field proton $T_1$ the satellites should be equal. This experiment has been carried out with acetamide and the results are displayed in figure VII.4.

It might be expected that if protons covalently bonded to
Figure VII. 4. Comparison between upper and lower satellites on acetamide $V_2$ at short and long uptimes.
a nitrogen were replaced by deuterons, there would be deuterium satellites at $\nu_d \pm \nu_b$. Deuterium satellites have indeed been found but they are not so well understood as proton satellites. They have not been observed in all compounds but when they are observed they provide invaluable information for use in assignment of nitrogen and deuterium lines.
The two deuterons in an \( \text{ND}_2 \) or \( \text{OD}_2 \) group have very similar electronic environments hence they should be expected to give quadrupole lines in the same frequency region. Naively one might expect in such a situation to observe a deuterium quadrupole spectrum of four lines, two \( J^+ \) 's and two \( J^- \) 's. This would be the case if the two deuterons were isolated but in an amino group or a water molecule where the deuterons are less than two angstroms apart and are bonded to the same atom, the interaction between them is not negligible and they must be treated as a two particle system. Experimentally it is found that the two deuteron system gives a quadrupole spectrum with 6 \( J^+ \) and 6 \( J^- \) lines as illustrated in figure VIII.1. It turns out that this behaviour can be predicted theoretically and in what follows the theory of two interacting deuterons in nearly identical sites will be developed and then used to attempt to extract the pure quadrupole splittings from the experimental data.

Figures VIII 2(a) and (b) show the energy level diagram of two isolated deuterons. In this system when an r.f. field is applied there are four frequencies at which allowed transitions can occur: 
\[
E(A^-) - E(O^-), \quad E(A^+) - E(O^+), \\
E(B^-) - E(O^-), \quad E(B^+) - E(O^+) 
\]
(neglecting \( J \) transitions). The effect of an interaction between the two deuterons is to push apart the pairs of nearly degenerate energy levels, 
\[
E(AO) \quad \text{and} \quad E(\overline{OA}), \\
E(BO) \quad \text{and} \quad E(\overline{OB}), \\nE(AB) \quad \text{and} \quad E(\overline{BA})
\]
as shown in figure VIII.2(c). The interaction causes a mixing of the state functions of the nearly degenerate levels and,
Figure VII. 1 (a) Deuterium fine structure in the ν-line of the...
Figure VIII.1 (b) Deuterium fine structure in the ν1 lines of the quadrupole spectrum of the water of hydration in L-serine hydrate.
Figure VIII.2. (a) The quadrupole-split energy levels of two isolated deuterons. (b) The combined energy level scheme with no interaction. (c) The effect of magnetic interaction upon pairs of nearly degenerate energy levels. (d) The resultant $V_+$ and $V_-$ spectra predicted by the set of energy levels (c).
as a result, transitions which were forbidden become allowed. There are six transitions in the $\nu^+$ region and the same number in the $\nu^-$ region as illustrated in figure VIII.2(d).

The starting point for a theoretical treatment of the fine structure on deuterium lines is the pure quadrupole Hamiltonian with the energies $\varepsilon(AA)$, $\varepsilon(AB)$, $\varepsilon(Bn)$, $\ldots$, $\varepsilon(00)$ along the diagonal. The state functions for each spin are in the principal axis system of its own electric field gradient. It will be assumed that any interaction between the deuterons will produce only off-diagonal matrix elements. Since most interaction mechanisms are of the form $I_1 I_2$ this is quite plausible. Clearly, since the quadrupole energies are so large in comparison, only those off-diagonal terms between nearly degenerate levels need be considered.

For a particular set e.g. $AO, OA$ the Hamiltonian is of the form:

$$
\begin{pmatrix}
\varepsilon(AO) & D \\
D^* & \varepsilon(OA)
\end{pmatrix}
$$

with eigenvalues

$$
E'(AO) = \frac{\varepsilon(AO) + \varepsilon(OA)}{2} + \frac{1}{2} \sqrt{\left(\varepsilon(AO) - \varepsilon(OA)\right)^2 + 4 |D|^2}
$$

$$
E'(OA) = \frac{\varepsilon(AO) + \varepsilon(OA)}{2} - \frac{1}{2} \sqrt{\left(\varepsilon(AO) - \varepsilon(OA)\right)^2 + 4 |D|^2}
$$

and eigenvectors (unnormalized)

$$
\lambda(E'(AO)) = \begin{pmatrix}
\frac{\varepsilon(AO) - \varepsilon(OA)}{2} & -D \\
\frac{\varepsilon(AO) - \varepsilon(OA)}{2} & \frac{\varepsilon(AO) - \varepsilon(OA)}{2} + \frac{1}{2} \sqrt{\left(\varepsilon(AO) - \varepsilon(OA)\right)^2 + 4 |D|^2}
\end{pmatrix}
$$

$$
\lambda(E'(OA)) = \begin{pmatrix}
\frac{\varepsilon(OA) - \varepsilon(AO)}{2} & D^* \\
\frac{\varepsilon(OA) - \varepsilon(AO)}{2} & \frac{\varepsilon(OA) - \varepsilon(AO)}{2} - \frac{1}{2} \sqrt{\left(\varepsilon(AO) - \varepsilon(OA)\right)^2 + 4 |D|^2}
\end{pmatrix}
$$

It is convenient to change to the notation:

$$
Q = \varepsilon(AO) - \varepsilon(OA), \quad S = \sqrt{Q^2 + 4 |D|^2}
$$
S is the energy splitting between $E'(AO)$ and $E'(OA)$. After normalization the eigenvectors of the new states become:

$$\lambda(E'(AO)) = \frac{1}{\sqrt{|D|^2 + (S - Q)^2/4}} \left( \begin{array}{c} b_1 \\ a_1 \end{array} \right)$$

$$\lambda(E'(OA)) = \frac{1}{\sqrt{|D|^2 + (S - Q)^2/4}} \left( \begin{array}{c} a_1 \\ -b_1^* \end{array} \right)$$

The eigenvalues and eigenvectors for the two other pairs of nearly degenerate levels have exactly analogous forms. For the $AB,BA$ levels the eigenvectors shall be written:

$$\left( \begin{array}{c} a_2 \\ b_2 \end{array} \right), \quad \left( \begin{array}{c} -b_2^* \\ a_2 \end{array} \right)$$

and for the $OB,BO$ levels:

$$\left( \begin{array}{c} a_3 \\ b_3 \end{array} \right), \quad \left( \begin{array}{c} -b_3^* \\ a_3 \end{array} \right)$$

The new state vectors are listed below in table 1

**TABLE VIII.1**

*Eigenvectors in the two deuteron system*

<table>
<thead>
<tr>
<th>Eigenvector</th>
<th>Eigenvector without interaction</th>
<th>Eigenvector with interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$</td>
<td>AA\rangle$</td>
<td>$</td>
</tr>
<tr>
<td>$</td>
<td>AB\rangle$</td>
<td>$</td>
</tr>
<tr>
<td>$</td>
<td>BA\rangle$</td>
<td>$</td>
</tr>
<tr>
<td>$</td>
<td>AO\rangle$</td>
<td>$</td>
</tr>
<tr>
<td>$</td>
<td>OB\rangle$</td>
<td>$</td>
</tr>
</tbody>
</table>

Now the relative transition probabilities can be calculated for the various transitions. An r.f. field along the x direction of the electric field gradient axes of one of the spins will induce the transition from $|AA\rangle$ to $|AO\rangle$ in that spin. First the transition at one of the two most intense $\nu +$ lines at frequency $\nu'(AO) - \nu'(OO)$ ($=\nu'(AA) - \nu'(OA)$) shall be considered. The transition probability $T_M$ is proportional to
where \((\hat{H}_x)_i = H \sin \Theta_i \cos \phi_i\) is the \(x\) component of the r.f. field for the "i"th spin. \(\Theta_i\) and \(\phi_i\) define the r.f. field directions relative to the principal field gradient axes of the \(i\)th spin. When \(T_m\) is averaged over all solid angles for a powder sample: 

\[
\overline{(H_x)_i} = \overline{(H_x)_2} \quad \text{and} \quad T_m \propto 2 \left( \overline{(H_x)_2} \right)^2
\]

In the \(v^+\) region of the spectrum there are four smaller subsidiary lines which can be separated into two pairs of equally intense lines: the more "allowed" pair \(1_{AB}^+ \leftrightarrow 1_{BB}^+\) and \(1_{BA}^+ \leftrightarrow 1_{BO}^+\) and the more "forbidden" pair \(1_{AB}^+ \leftrightarrow 1_{BO}^+\) and \(1_{BA}^+ \leftrightarrow 1_{BB}^+\). The names more "allowed" and more "forbidden" are derived from the fact that in the absence of an interaction to mix the states one pair of transitions would be allowed and the other pair would be forbidden. The transition probability of the more allowed pair is proportional to:

\[
T_{A+} \propto |\langle AB \mid H \cdot I \mid BO \rangle|^2
\]

\[
= |(b_2^* \langle AB \mid + a_2 \langle BA \mid) H \cdot I (a_3 \langle BO \rangle - b_2^* \langle OB \rangle)|^2
\]

\[
= 1 - b_2^* b_2 (H_x)_1 + a_2 a_3 (H_x)_2|^2
\]

Averaging over all solid angles this becomes:

\[
T_{A+} \propto a_2^2 a_3^2 (H_x)_2^2 + |b_2|^2 |b_3|^2 (H_x)_1^2 - (b_2^* b_2 + b_2 b_2^*) a_2 a_3 (H_x)_1 (H_x)_2
\]

Similarly the transition probability of the more forbidden pair is proportional to:

\[
T_{F+} \propto |b_2|^2 a_3^2 (H_x)_1^2 + a_2^2 |b_3|^2 (H_x)_2^2 + (b_2^* b_2 + b_2 b_2^*) a_2 a_3 (H_x)_1 (H_x)_2
\]
Since the proportionality constants are the same for these three types of transitions, it is easy to show that:

\[ T_{A+} + T_{F+} = \frac{1}{2} T_{M} \]

indicating that the sum of the intensities of a more "allowed" subsidiary line and a more "forbidden" subsidiary line should be one-half the intensity of one of the main \( V+ \) transitions. This has indeed been observed experimentally, however since the lines are quite weak it is difficult to measure accurately their intensities. This property also holds for the subsidiary \( V- \) lines and it can be proven in an analogous manner.

To obtain more explicit values for the transition probabilities of the subsidiary lines it is necessary to calculate the averages of the quantities \( \sin \theta \cos \phi \) over all solid angles for the two spins. The averages \( \langle H_x \rangle_1^2 \) and \( \langle iix \rangle_2^2 \) are simply

\[ \langle H_x \rangle_1^2 = \frac{1}{4\pi} \int_{0}^{\pi} \int_{0}^{2\pi} \sin \theta \cos \phi \sin \theta \cos \phi \sin \theta d\theta d\phi = \frac{1}{2} \]

However the quantity \( \langle H_x \rangle_1 \langle iix \rangle_2 \) is more difficult to calculate since it depends upon the relative orientations of the electric field gradients of the two deuterons. The orientations used here are based on a deuterium magnetic resonance study of a series of \( \lambda\)-O-D's by T. Chiba (30). Chiba has found that the z axis of the field gradient is usually less than 3 degrees from the OD bond direction and that the Y axis is usually within 15 degrees of the normal to the plane defined by X-O-D. With this choice of axes, as illustrated in figure VIII.3, if the x component of the r.f. field at one of the spins is \( \sin \theta \cos \phi \), at the other spin it should be \(- (\sin \theta \cos \phi \cos \Delta - \cos \phi \sin \Delta) \) where \( \Delta \) is the
Figure VIII.3. Electric field gradient axes for the deuterons in an OD₂ or NH₂ group from (15). The X'-Y'-Z' coordinate system is used for the calculation of the dipolar interaction matrix elements. The angle ₀ is used for the calculation of the proton-deuteron interaction in Chapter IX.
angle between the z field gradient axes of the two spins. Then the required average is:

\[
\langle \frac{\hat{H}_2(\hat{H}_2)}{\mu^2} \rangle = \frac{1}{4\pi} \int_{0}^{2\pi} \int_{0}^{\pi} \sin \theta \cos \phi (-\sin \theta \cos \theta \cos \Delta - \cos \theta \sin \Delta) \sin \theta \cos \phi \cos A \, d\theta \, d\phi
\]

\[
= -\frac{\cos \Delta}{3}
\]

This makes it possible to write expressions for the transition probabilities of the more allowed and more forbidden \( \nu^+ \) subsidiary lines:

\[
T_A \propto a_1^2 a_3^2 + |b_1|^2 |b_2|^2 + \cos \Delta (b_2^* b_2 + b_2 b_2) a_2 a_3
\]

\[
T_F \propto |b_2|^2 a_1^2 + a_2^2 |b_2|^2 - \cos \Delta (b_2^* b_2 + b_2 b_2) a_2 a_3
\]

The preceding calculations for the transition probabilities of the \( \nu^+ \) subsidiary lines can be repeated for the \( \nu^- \) subsidiary lines. In this case the transitions are induced by the \( \nu \) components of the r.f. field which differ in sign for the two spins. The results are

\[
T_A - \propto a_1^2 a_2^2 + |b_1|^2 |b_2|^2 - (b_1 b_2^* + b_1^* b_2) a_1 a_2
\]

\[
T_F - \propto a_2^2 |b_1|^2 + a_2^2 |b_1|^2 + (b_1 b_2^* + b_1^* b_2) a_1 a_2
\]

The above expressions give the intensities of the subsidiary lines relative to the main lines as a function of the measured splittings \( S \), the pure splittings in the absence of mixing \( Q \) and the interaction matrix elements \( D \). There are three values for each of \( S \), \( Q \), and \( D \), one value for each set of nearly degenerate energy levels and within a particular set of levels they are related by \( S = \sqrt{\alpha^2 + 4 |b|^2} \). Because relative heights are a difficult quantity to measure accurately and it is not easy to manipulate the algebra such that the matrix elements \( D \) can be extricated from the other quantities, values for \( D \) produced from a theoretical approach.
were applied to the above expressions and the predicted and experimental heights were compared.

The interaction between the two deuterons in an HD₂ or an OD₂ group stems primarily from the coupling of their magnetic dipole moments. The dipolar interaction can have two mechanisms, direct coupling or indirect coupling through the electrons.

The indirect coupling of the two nuclei through the electrons is of the form \( A_1 A_2 \gamma_1 \gamma_2 C \) where \( A_1 A_2 \) are hyperfine interaction constants, \( \gamma_1, \gamma_2 \) are the gyromagnetic ratios of the nuclei and C is a constant \( (16 \text{ page 30}) \). The hyperfine interaction constants A vary as the cube of the nuclear charge "seen" by the valence electrons so they should be expected to be very small for small atoms like deuterium. Since the deuteron gyromagnetic ratio is also small, the indirect dipolar interaction is not expected to make a significant contribution to the interdeuteron interaction. The magnitude of the indirect interaction in HD has been found to have the negligibly small value of 43Hz \( (37) \).

The direct dipolar coupling between two deuterons less than 2 angstroms apart can be considerable and it shall be calculated now. Since the principal axes of the electric field gradients of the two spins are not coincident it is convenient to re-express the state functions of the spins in a common co-ordinate system before the dipolar operator is applied. When using the Van Vleck expansion of the dipolar operator it is usually worthwhile to choose a co-ordinate system in which the greatest number of terms vanish. This is satisfied by the system \( x'y'z' \) in figure VIII.3.
It is a property of spin 1 wave functions that the three linear combinations \(-1/\sqrt{2} (|\uparrow\rangle - |\downarrow\rangle) = -|B\rangle\), \(\sqrt{2} (|\uparrow\rangle + |\downarrow\rangle) = (|A\rangle, |0\rangle)\), transform under rotations like x y and z. Then, if these functions are used, the simple cartesian co-ordinate rotation matrices may be used to represent a state function in a new co-ordinate system. In the case at hand, to make use of the new common co-ordinate system \(x' y' z'\), the basis functions of of deuteron number 1 must be rotated by \(\Delta/2 + 90\) about the \(y'\) axis and for deuteron number 2 a rotation of \(180\) about \(z_2\) followed by a \(90-\Delta/2\) rotation about the new \(y'\) axis is required. The new representations of the state functions in terms of the state functions along the common co-ordinate axes system axes are listed below:

\[
\begin{align*}
|B\rangle' &= -\sin\Delta/2 |B\rangle - \cos\Delta/2 |0\rangle \\
|A\rangle' &= |A\rangle \\
|0\rangle' &= \cos\Delta/2 |B\rangle - \sin\Delta/2 |0\rangle \\
|B\rangle'_2 &= -\sin\Delta/2 |B\rangle + \cos\Delta/2 |0\rangle \\
|A\rangle'_2 &= -|A\rangle \\
|0\rangle'_2 &= \cos\Delta/2 |B\rangle + \sin\Delta/2 |0\rangle \\
\end{align*}
\]

Sample rotation of co-ordinates:

\[
-|B\rangle' =\begin{pmatrix}
\cos(90-\Delta/2) & 0 & -\sin(90-\Delta/2) \\
0 & 1 & 0 \\
\sin(90-\Delta/2) & 0 & \cos(90-\Delta/2)
\end{pmatrix}
\begin{pmatrix}
-1 & 0 & 1 \\
0 & -1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
\sin\Delta/2 \\
0 \\
-\cos\Delta/2
\end{pmatrix}
\]

with this choice of axes, only the first two terms (\(\Delta N = 0\)) of the Van Vleck expansion of the dipolar operator are non-zero. The operator has the form

\[
\mathcal{H}_{00} = \hbar \gamma^2 \left( -2I_{11}I_{22} + \frac{1}{2}(I_{11}I_{-2} + I_{-1}I_{22}) \right)
\]

This leads to the matrix elements:
\[ D_{AO} = \frac{\langle A | \chi_0 | \chi_0 | A \rangle}{r_{00}^3} = \frac{\gamma_0^3}{r_{00}^3} \left( 2 \cos^2 \Delta/2 + \sin^2 \Delta/2 \right) \]

\[ D_{AB} = \frac{\gamma_0^3}{r_{00}^3} \left( 2 \sin^2 \Delta/2 + \cos^2 \Delta/2 \right) \]

\[ D_{BO} = -\frac{\gamma_0^3}{r_{00}^3} \]

The above calculation was repeated with the Y axes of each of the spins tilted about the Z axis by 10°. The resulting change in magnitude of the matrix elements was small (about 10% difference in \( D_{AB} \) and smaller differences in \( D_{AO} \) and \( D_{BO} \)) and it made little difference whether the two Y axes were tilted towards or away from each other.

In table VIII.2 the experimental splittings \( S \) and calculated matrix elements \( D \) are listed for a series of deuterated amides and for L-serine hydrate. In the calculation of the matrix element the distance between the two deuterons was taken as 1.9 angstroms for the amides and 1.55 angstroms for the L-serine hydrate (\( \gamma_0^3 \)). In table VIII.3 the experimental line intensities are compared with the transition probabilities calculated using the values of \( S \) and \( D \) from table VIII.2.

The agreement between calculated and experimental subsidiary line intensities is not particularly good; however this may be partly due to experimental error. But the fact that there is some correlation does indicate that the direct dipolar interaction could account for the experimental spectra.

If theory and experiment had agreed perfectly, it would be possible to reliably assign the \( \gamma^+ \) and \( \gamma^- \) lines to each other. Unfortunately in the present situation assignments
### TABLE VIII.2
Experimental splittings and calculated matrix elements in deuterium fine structure. All numbers are represented in KHz.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$S_{A0}$</th>
<th>$S_{AB}$</th>
<th>$S_{BO}$</th>
<th>$D_{A0}$</th>
<th>$D_{AB}$</th>
<th>$D_{BO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetamide 77K</td>
<td>1.28 (.1)</td>
<td>2.80 (.2)</td>
<td>2.28 (.1)</td>
<td>.52</td>
<td>.76</td>
<td>-.425</td>
</tr>
<tr>
<td>acetamide 295K</td>
<td>1.35 (.1)</td>
<td>3.2 (.2)</td>
<td>3.3 (.1)</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>nicotinamide 295K</td>
<td>8.7 (.2)</td>
<td>1.9 (.2)</td>
<td>6.8 (.2)</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>propionamide 295K</td>
<td>4.7 (.2)</td>
<td>1.8 (.2)</td>
<td>3.7 (.2)</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>thioacetamide I 295K</td>
<td>4.8 (.2)</td>
<td>3.15 (.2)</td>
<td>7.2 (.2)</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>thioacetamide II 295K</td>
<td>1.4 (.2)</td>
<td>3.95 (.2)</td>
<td>4.1 (.2)</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>L-serine hydrate 77K</td>
<td>3.25 (.1)</td>
<td>2.4 (.2)</td>
<td>3.00 (.1)</td>
<td>1.0</td>
<td>1.23</td>
<td>-.72</td>
</tr>
</tbody>
</table>

### TABLE VIII.3
Experimental and theoretical line intensities in deuterium fine structure.

<table>
<thead>
<tr>
<th>Compound</th>
<th>subsidiary line intensity</th>
<th>main line intensity</th>
<th>calculated transition probabilities</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>outer</td>
<td>inner</td>
<td>outer</td>
</tr>
<tr>
<td>acetamide 77K</td>
<td>.19</td>
<td>.81</td>
<td>.79</td>
</tr>
<tr>
<td>acetamide 295K</td>
<td>.10</td>
<td>.90</td>
<td>.90</td>
</tr>
<tr>
<td>nicotinamide 295K</td>
<td>.8</td>
<td>.2</td>
<td>.65</td>
</tr>
<tr>
<td>propionamide 295K</td>
<td>.68</td>
<td>.32</td>
<td>.42</td>
</tr>
<tr>
<td>thioacetamide I 295K</td>
<td>.1</td>
<td>.9</td>
<td>.9</td>
</tr>
<tr>
<td>thioacetamide II 295K</td>
<td>.1</td>
<td>.9</td>
<td>.9</td>
</tr>
<tr>
<td>L-serine hydrate 77K</td>
<td>.6</td>
<td>.4</td>
<td>.82</td>
</tr>
</tbody>
</table>
are somewhat ambiguous.

Assuming the theory is correct, the pairing of $\nu^+$ and $\nu^-$ lines may be carried out in the following way. The $E(A0)$ level is defined to be the upper of the two main $\nu^+$ lines. The calculations in table VIII.3 indicate whether the more intense of the subsidiary lines corresponds to the "allowed" or the "forbidden" transition (in all but one compound, L-serine hydrate, the "allowed" transition is the more intense of the two). With this information, the knowledge of which subsidiary lines on $\nu^-$ are the larger, the inner or the outer ones, makes it easy to determine which is the higher energy level, $E(AB)$ or $E(BA)$. Then the higher energy level of $E(B0)$ and $E(0B)$ can be found using the same procedure with the $\nu^+$ subsidiary lines. For example, in acetamide at 77 $\AA$, since the allowed transitions are more intense and the inner $\nu^-$ subsidiary lines are larger than the outer ones $E(BA)$ is at a higher energy than $E(AB)$. Then, because the outer subsidiary lines on $\nu^+$ are larger than the inner ones $E(BO)$ must be at a higher energy than $E(0B)$.

In table VIII.4 are listed the pure quadrupole frequencies of the two deuteron systems produced from the above assignment method. Since, if the calculation of matrix elements is wrong, this presentation would be artificial, the average values of $e^2 q\eta^2$ and $\eta$ for the two sites are given as well.

It is interesting that in all cases $E(B0)$ was predicted higher in energy than $E(0B)$ and in all cases but two, propionamide and L-serine hydrate, $E(AB)$ was predicted to have a higher energy than $E(0B)$. 
Quadrupole constants for the fine structure sites

**TABLE VIII.4**

<table>
<thead>
<tr>
<th>Compound</th>
<th>site I $\varepsilon^2 q\eta$</th>
<th>$\eta$</th>
<th>site II $\varepsilon^2 q\eta$</th>
<th>$\eta$</th>
<th>mean of the two sites $\varepsilon^2 q\eta$</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetamide 77A</td>
<td>196.3</td>
<td>.161</td>
<td>194.4</td>
<td>.173</td>
<td>195.3</td>
<td>.167</td>
</tr>
<tr>
<td>acetamide 295K</td>
<td>198.2</td>
<td>.143</td>
<td>195.4</td>
<td>.164</td>
<td>196.8</td>
<td>.154</td>
</tr>
<tr>
<td>nicotinamide 295K</td>
<td>207.1</td>
<td>.163</td>
<td>197.6</td>
<td>.152</td>
<td>202.0</td>
<td>.157</td>
</tr>
<tr>
<td>propionamide 295K</td>
<td>199.3</td>
<td>.146</td>
<td>193.7</td>
<td>.139</td>
<td>196.5</td>
<td>.142</td>
</tr>
<tr>
<td>thioacetamide I 295K</td>
<td>202.7</td>
<td>.130</td>
<td>194.8</td>
<td>.160</td>
<td>198.8</td>
<td>.145</td>
</tr>
<tr>
<td>thioacetamide II 295K</td>
<td>197.2</td>
<td>.123</td>
<td>193.8</td>
<td>.154</td>
<td>195.4</td>
<td>.138</td>
</tr>
<tr>
<td>L-serine hydrate 77K</td>
<td>240.0</td>
<td>.110</td>
<td>236.5</td>
<td>.110</td>
<td>238.6</td>
<td>.110</td>
</tr>
</tbody>
</table>
The fine structure pattern in the spectrum of 4-amino-n-butyric acid hydrate represents another degree in complexity of the two nearly equivalent deuterons problem. In this compound not only are the pairs $E(AO), E(OA)$ and $E(BO), E(OB)$ nearly degenerate but also the $E(OA)$ level is close to the $E(BO), E(OB)$ pair. The resulting mixtures of states are more complicated to analyse and they shall not be treated here.

The problem of 3 nearly equivalent deuterons in an $ND_3$ site is also very complex. Experimentally, the lines usually overlap to such an extent that it is impossible to measure accurate frequencies of the quadrupole lines. No attempt has been made to analyse this situation theoretically.
Chapter IX. Spectra from Partially deuterated samples.

In aqueous solution when a hydrogen is bonded to an atom with a high electronegativity (e.g. O, N, S, Cl) it undergoes a continuous exchange process with hydrogen atoms in the solution, but if it is bonded to an atom with a low electronegativity (e.g. C) it does not usually undergo any exchange. Consequently, the procedure used for deuterating compounds in this laboratory, repeated recrystallization from D$_2$O solution, produces a compound with deuterons on the more electronegative sites but with protons on the less electronegative sites. A considerable number of the compounds that were deuterated contained carbons with attached hydrogens so they were directly amenable to quadrupole resonance by the laboratory frame double resonance method. However there are many compounds which have no inexchangeable proton sites e.g. water, urea, some inorganic hydrates. To make it possible to use our method for these compounds some protons have to be left on, thus resulting in the making of a 'partially deuterated' sample in which a specific hydrogen site may contain either a deuteron or a proton. The quadrupole spectrum of such a compound can be different from that in the pure compound and in this chapter the effects of partial deuteration on quadrupole spectra will be pointed out and some effort will be made to give an explanation for them.

When nitrogen compounds are deuterated, a regular shift is found in the nitrogen quadrupole frequencies (see Chapter X) and it can be accounted for by a change in electron occupation along the NH bonds (29). In a partially deuterated
sample the spectrum contains a set of lines for each nitrogen combination in the sample. In an NH₂ site an ND line is usually found roughly midway between the NH₂ and ND lines as illustrated in figure IX.1. Since the nitrogen quadrupole spectra can be obtained unambiguously from the undeuterated compound and the isotope shifts in frequency play a minor role in this thesis, this topic will not be discussed further.

Although the substitution of a proton for a deuteron in an OD₂ or ND₂ should have a negligible effect on the actual value of the electric field gradient at the opposite site, nevertheless the quadrupole spectrum of the remaining deuteron is found to be different (see figure IX.2). It is known (39) that crystal structures change by negligibly small amounts when the protons are replaced by deuterons. Two possible sources of this change in the quadrupole spectrum are an alteration of the vibrational modes of the deuteron and a direct dipolar interaction between the deuteron and the proton.

Even at very low temperatures the deuteron in an OD₂ or ND₂ is continuously vibrating with a trajectory and frequency determined by several factors including the temperature, strength of bond, and the molecular and crystal structure. Since the vibrational frequencies are very fast compared with the time of a quadrupole measurement, the measured quadrupole constants will represent a tensor average of the effective field gradient the deuteron "sees" along its spin axes over a period of time long compared with the resonance experiment. If the amplitude and frequency of the vibrations
Figure IX.1. The ν₂ lines in a partially deuterated acetamide sample with a D/H ratio of 1:3 on the NH₂ group.
change there will be a corresponding change in the measured quadrupole constants. In an OD$_2$ or ND$_2$ group the deuterons undergo coupled modes of oscillation which are altered if a deuteron is replaced by a proton, so the quadrupole spectrum from the remaining deuteron might be expected to be different.

The various vibrational frequencies of a deuteron can be measured by infrared spectroscopy. In Ice Ih at 100 K no difference in the OD along the bond stretching frequency was detected between OD$_2$ and OH$_2$ (40) but a 20% change was found in a rotational vibrational frequency. Then it would appear that in Ice Ih the OD stretching modes do not affect the measured quadrupole constants but this may not be true for the rotational modes of vibration. Unfortunately, due to lack of facility, a quantitative prediction of the change in quadrupole spectra resulting from motional effects shall not be undertaken but the fact the vibrational frequencies are not changed very much indicate that the change in the tensor average of the field gradient is small.

A calculation has been made of the direct dipolar interaction between a proton and a deuteron and it shows, qualitatively at least, that the pure dipolar interaction could account for the observed change in the quadrupole spectrum on deuteration.

The deuteron in an OH$_2$ or NH$_2$ in zero field shall be given the Hamiltonian:

\[ \mathcal{H} = \mathcal{H}_{\text{quadrupole}} + \mathcal{H}_{\text{dipolar}} \]

The most convenient axes of quantization to use are the electric field gradient axes at the deuteron site. As in
Chapter VIII the Z axis shall be assumed to be along the OD bond and the X and Y axes parallel and perpendicular to the OHD plane (see figure VIII.3). The angles for the dipolar operator are then $\Theta, \Phi, \Theta$. The following Hamiltonian is obtained (with the basis states $|A, \frac{1}{2}\rangle$, $|A, -\frac{1}{2}\rangle$, $|B, \frac{1}{2}\rangle$, $|B, -\frac{1}{2}\rangle$, $|0, \frac{1}{2}\rangle$, $|0, -\frac{1}{2}\rangle$)

$$H = \frac{e^2 qQ}{4} \begin{pmatrix} (1 + \eta) & 0 & A_d & B_d & 0 & C_d \\ 0 & (1 + \eta) & B_d & 0 & C_d & -B_d \\ -A_d & -B_d & (1 - \eta) & 0 & 0 & D_d \\ B_d & 0 & 0 & (1 - \eta) & D_d & 0 \\ C_d & -B_d & -D_d & 0 & 0 & -2 \\ D_d & 0 & -D_d & 0 & 0 & -2 \end{pmatrix}$$

where $A_d = \frac{R}{2}(1 - 3 \cos^2 \Theta)$, $B_d = -\frac{1}{2}R \sin 2\Theta$, $C_d = R\left(-\frac{1}{4} + \frac{3}{4} \cos 2\Theta\right)$, $D_d = R/2$, $R = \sqrt{\left(\frac{\hbar}{\Delta \Delta'}\right)^2 / \left(\frac{e^2 qQ}{4}\right)}$

These matrix elements were calculated for two experimental situations: the water of hydration of L-serine hydrate and the amide group of acetamide. Using a matrix diagonalization computer program the energy eigenvalues and the new transition frequencies were generated.

With no interacting proton, or deuteron, a deuteron has a three energy level system. The effect of the dipolar interaction with a nearby proton is to split each of these into two. This means that instead of a single $V^+$ and a single $V^-$ in the spectrum one would expect four $V^+$ lines and four $V^-$ lines (assuming all transitions are allowed). A stick diagram of the new "HD" transitions calculated from the Hamiltonian is shown in figure IX.3. For acetamide the N-H distances were assumed to be 1 angstrom. The values of .93
Figure IX. 2. The quadrupole spectra of the water molecule in partially deuterated L-serine hydrate and partially deuterated acetamide. The arrows mark the pure deuterium quadrupole frequencies.
Figure IX.3. The positions of the calculated $^1$H$^2$O transitions in the water molecule of L-serine hydrate and in acetamide. The arrows mark the pure deuterium quadrupole lines.
angstrom and .96 angstrom from the structure paper (41) were determined from X-ray techniques which tend to underestimate N-H distances.

The agreement with the experimental data is qualitatively satisfactory. Because the "HD" lines are close together, they overlap producing broad bumps. For acetamide the bumps are very near the predicted position but in L-serine hydrate the predicted "HD" lines are further from the pure deuterium lines than those in the experimental spectrum. A less encouraging feature of this calculation is the fact that the magnitude and direction of the "IID" shift is quite dependent on the HD distance and so that slight changes in the crystal structure could lead to fairly different results. nevertheless it is clear that the dipolar interaction could account for the shift in frequency between DD and HD pairs.

It should be pointed out that in HD pairs the mutual interaction may lead to an increased sensitivity with the laboratory frame double resonance method tending to make "HD" lines artificially bigger than DD lines. This effect has been observed in ice Ih (see Chapter XIII).

The evidence, both theoretical and experimental, indicates that for a simple OD group or ND group with no nearby hydrogens the quadrupole spectrum for a partially deuterated sample is very similar to that from a fully deuterated one.
Chapter X. Sample Preparation, Operational Procedures and Assignment of Lines.

The laboratory frame double resonance method has been in operation only a few years so the optimum technique of operation for maximum resolution and highest efficiency may not yet have been established. The current state of the art as employed for and developed during the research for this thesis shall be related here. This account will deal first with the preparation of samples and then the obtaining of the spectra and the assignment of quadrupole lines shall be discussed.

Almost all the samples used for this thesis research were obtained from British Drug Houses. Most of the undeuterated samples were used straight from the bottle without purification.

In a few samples, including L-hydroxyproline and Y-glycine, the proton free induction decay was marred by a large noisy transient which made it impossible to measure proton magnetization. The explanation is that the samples were composed of piezoelectric crystals. The electric fields produced by the high power 90° pulse introduced mechanical stress to the crystal. In the relaxation of this stress there is an emission of voltages which may be picked up by the receiver of the free induction decay signal. The extent of the mechanical stress which can be induced and the intensity of the response voltage are greater if the frequency of the driving electric field (and also the phase sensitive detection reference frequency) is near a resonant frequency of
the piezoelectric crystal. Since the resonant frequency is a function of the crystal size it can be changed by changing the size of the crystal. In this way, the L-hydroxyproline and \( \gamma \)-glycine samples worked well after having been ground finely with a mortar and pestle.

In some compounds, proton T1's have been so long that the length of time to do a quadrupole resonance experiment would be prohibitively long. The T1 of formamide, which had been over 5 minutes long, was reduced to one or two minutes by dissolving in it a paramagnetic impurity, copper acetate. The T1 of L-alanine was also decreased by recrystallization from an aqueous solution containing paramagnetic ions. Another way to lower the T1 of the sample is to irradiate it with x-rays to create paramagnetic centres. In all these cases it is important to keep the impurity concentration small so that it does not alter the quadrupole spectrum.

If a sample has a very short proton T1, there are at least two ways of lengthening it. If the T1 arises from molecular motion it is a strong function of temperature and by maintaining the apparatus at a different temperature - either lower or higher than 77K - it is possible that the T1 may be lengthened to an acceptable value. Thioacetamide, which has a very short T1 at 77K was found to have a fairly long T1 at room temperature. If the proton T1 is caused by the presence of paramagnetic impurities it may be possible to remove the impurities by "washing" the sample in successively more dilute aqueous solutions of ethylenediaminetetra-acetic acid di sodium salt. The use of this reagent, EDTA, which removes ions by complexing with them, raised the proton T1 of
bovine achilles tendon collagen from about ½ second to nearly 3 seconds - unfortunately still too short to run.

Most of the samples which were deuterated were soluble in water. In aqueous solution hydrogens bonded to nitrogen and oxygen atoms undergo exchange with the hydrogen atoms in water. Then, hydrogen bonding sites can be deuterated by repeated recrystallization in D₂O. The 99.8% pure D₂O was purchased from Norsk Hydro Ltd. Usually 2 to 3 recrystallizations were sufficient for obtaining good nitrogen and deuterium spectra. The effect of partial deuteration after only one recrystallization was very prominent in both types of spectra and has been discussed in Chapter IX.

The recrystallization process sometimes produced hydrates. In several cases, e.g. L-serine and L-proline, hydrates were formed if the recrystallization was carried out quickly by boiling off most of the D₂O but the anhydrous form resulted from slow recrystallization in a vacuum dewar. In all cases the anhydrous form could be recovered from the hydrate by heating in an oven.

The HCl co-crystals of some compounds were formed by dissolving the sample in sufficient aqueous HCl solution and letting the water evaporate off in the oven. In certain cases the pure compound was not soluble in water but its HCl co-crystal was. Then the HCl co-crystal can be deuterated and the HCl removed by reaction with a carbonate such as K₂CO₃. This method was used to deuterate L-tyrosine and L-histidine.

Although indole is insoluble in water it is quite soluble in ethyl alcohol. Partial deuteration of the α-H site of
indole was carried out by dissolving the sample in a mixture of D$_2$O and ethyl alcohol.

Since the population difference in the quadrupolar nuclei at the beginning of the uptime is proportional to the magnetization of the protons before the first set of level crossings, it is clearly important to leave the protons in the high field until they are well aligned. This is achieved, practically, after 3 or 4 proton T$_1$'s. From this point on the mechanisms of nitrogen and deuterium quadrupole resonance are quite different so they shall be treated separately.

Because the sensitivity of the apparatus to nitrogen quadrupole resonance is independent of the proton magnetization remaining at the end of the uptime, the length of uptime for nitrogen resonance is not very critical provided the nitrogen zero field T$_1$ is long. However, if very short times are used the amount of power absorbed by the sample will be reduced and if very long times are used there is a danger of the sample chamber becoming clogged with ice. The usual uptime employed is 5 seconds.

The task of obtaining a quadrupole spectrum is divided into two parts - finding the approximate regions of the quadrupole lines and resolving each quadrupole line at the highest resolution. Often it is possible to save a lot of time by using a knowledge of the systematics of nitrogen quadrupole spectra to explore specific regions of the spectrum where lines are expected. For example, in NH$_3$ sites there are rarely any lines above 1500 Hz and in amides the
NHz \textsuperscript{V} is almost always in the range 1800 to 2500 KHz. When searching for lines over a big range it has been found practical to cover large regions of frequency each cycle, the most common procedure being to use a 5 second uptime to scan 50 KHz in 1 KHz steps. This should be carried out with no applied magnetic field at position 2 since the proton satellites will then be close to the quadrupole lines and will contribute to the depth of absorption. Relatively high r.f. powers, typically 1-4 gauss peak to peak, are used when searching for nitrogen quadrupole lines. Once the spectrum has been obtained to within 50 KHz it is a simple matter to define the lines to within 10 or 20 KHz by using a smaller scan size each cycle.

The procedure used, from this point on, for achieving maximum resolution of the spectrum depends on the type of nitrogen line being tackled. For a narrow line with a deep absorption the immediate frequency region is stepped through at the rate of 0.5 or 1 KHz per cycle using r.f. powers of order one half gauss peak to peak or less to eliminate any absorption from proton satellites. Since the narrowest nitrogen lines have widths of a few KHz this process is adequate for accurate definition of the spectrum.

Unfortunately, however, not all nitrogen lines are strong and narrow. The first way to improve the signal from a broad weak line is to increase the power and also, if it helps, to scan a small range of frequencies rather than to irradiate at only one frequency per cycle. Since the increased power will excite proton satellites it shall be necessary to apply a magnetic field large enough to move
them aside. Obviously this measure need not be taken in a deuterated sample where there are no proton satellites. If a line is still unresolvable after this, three further ways are available to improve the signal to noise.

In some cases a measurable absorption is found only by sweeping 5 or 10 KHz per cycle and when this has happened a technique of staggering sweeps has often been used successfully. The process consists of making relatively large sweeps of 5-10 KHz and incrementing the starting frequency of the sweep by 1 or 2 KHz each cycle. When even this technique is incapable of increasing the signal above the noise, as a last resort it is sometimes possible to improve the resolution by adding up a series of successive scans through the region of the line. This method has been used only very rarely.

In Chapter V, it was shown that in nitrogen quadrupole resonance, all the accessible proton signal can be destroyed by irradiating a $V^+$ line but irradiation on a $V^-$ or $V_0$ line can at best reach only about one-third of the useful proton magnetization. Where $V_0$ is larger than the low frequency proton linewidth and $V^+$ is resolvable, this inherent sensitivity of the apparatus can be improved considerably by applying a second r.f. field to increase the population difference in the quadrupole levels of interest. A $V^-$ line can be made much more intense if a second r.f. field at saturation power is applied to the centre of the $V_0$ line at the same time as the first field steps through the region where $V^-$ is expected at much lower power. The inverse process works for $V_0$. This double irradiation is achieved in our
apparatus with only one coil and a low frequency relay which switches between the two r.f. fields. The double irradiation procedure has been successfully used to determine $\gamma$ and $\gamma_0$'s in many nitrogen compounds.

Because the sensitivity of the laboratory frame double resonance technique to deuterium lines is very dependent on the amount of proton alignment remaining at the end of the irradiation period, it is important to use the shortest uptime that is practical: 2 seconds is the time commonly used. Deuterium quadrupole resonance spectra have always been found to occur between 80 and 200 kHz. Very often, especially in compounds with NB3 groups, several lines are so close together resolution is impossible and only a broad irregular absorption can be produced. Under high powers of irradiation the low frequency proton spectrum can extend up to 200 KHz or more so it is very important to use low powers. 5 KHz scans at about 100 milligauss peak to peak are commonly used to search for deuterium lines. Then to resolve a good spectrum an r.f. field of 50 milligauss or less stepped at 0.1 KHz per cycle is employed. The magnetic field at position 2 must be maintained accurately at zero since even quite small fields broaden and shift the low $\gamma$ deuterium lines. Double irradiation does not work for deuterium resonances.

The art of extracting quadrupole constants from a quadrupole spectrum will now be elaborated upon. Clearly if there is only one quadrupolar nucleus in the compound being studied there is no problem in assignment, however, if compounds
have two or more inequivalent quadrupolar nuclei of the same type the task of assigning the lines becomes more difficult. There are two aspects to this task: first the lines must be separated into $\nu_\text{+}$, $\nu_\text{-}$, $\nu_0$ groups and then each group must be assigned to a particular site in the compound. Since nitrogens and deuterons give quite different spectra the methods of dealing with them will be treated separately.

When nitrogen NQR is carried out by the laboratory frame double resonance method, it is often possible to see all three lines of a $\nu_\text{+}$, $\nu_\text{-}$, $\nu_0$ group so the relation $\nu_\text{+} = \nu_\text{-} + \nu_0$ can be used to separate the lines into groups. If it is not obvious which lines are $\nu_\text{+}$'s and which are $\nu_\text{-}$'s a DC magnetic field can be applied at position 2. The effect of a magnetic field on a powder sample is to asymmetrically broaden $\nu_\text{+}$'s in the direction of increasing frequency and asymmetrically broaden $\nu_\text{-}$'s in the direction of decreasing frequency (5). Fields of 40 gauss or more are required to make this effect observable with nitrogens. In some compounds, e.g. thioacetamide, the nitrogens in two inequivalent sites have different spin-lattice relaxation times. When this happens, the intensity of the quadrupole lines of the nitrogen with the faster relaxation times will be less than that of the other and this can be used to separate the lines. In compounds where it can be applied, double irradiation is an excellent method of distinguishing which lines belong to a particular group. If a $\nu_0$ is irradiated at saturation intensity, the sensitivity of the method to the matching $\nu$- transition is vastly improved but the sensitivity to any other transition is unchanged.
Because the values of $e^2qQ$ and $\eta$ observed in some classes of nitrogen site fall within a relatively small range, quadrupole lines can often be assigned to particular nuclei on this basis. When hydrogens bonded to a nitrogen are replaced by deuterons a shift occurs in the quadrupole frequencies of the nitrogen. These shifts are similar for nitrogens in similar bonding configurations and can be of assistance in the assignment of lines. These isotope shifts have been considered in some detail in reference (29). The normal ranges of quadrupole constants and the isotopic shifts for three of the more commonly found nitrogen bonding configurations are listed in Table X.1.

<table>
<thead>
<tr>
<th>Site</th>
<th>$e^2qQ$ range (KHz)</th>
<th>$\eta$ range</th>
<th>Isotopic shift range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amide NH$_2$</td>
<td>1900 to 2550</td>
<td>0.3 to 0.5</td>
<td>+20 to +30</td>
</tr>
<tr>
<td>Tetrahedral N$^+$H$_2$</td>
<td>1250 to 1650</td>
<td>0.85 to 1</td>
<td>-10 to -30</td>
</tr>
<tr>
<td>Amino acid N$^+$H$_3$</td>
<td>1050 to 1400</td>
<td>0 to 0.5</td>
<td>-10 to -30</td>
</tr>
</tbody>
</table>

When very high powers of irradiation are used satellites at $\nu_n \mp \nu_0$ can sometimes be observed in deuterated nitrogen compounds. If this occurs it gives a positive assignment of a set of deuterium lines to a set of nitrogen lines. This has been valuable in the analysis of L-serine hydrate where the ND$_3$ lines were linked with the corresponding nitrogen lines (see figure X.1).

Proton satellites may also be used to assign nitrogen lines as discussed in chapter VII. In a good spectrum NH, NH$_2$, and NH$_3$'s can sometimes be distinguished but since the distinction between these three situations is not very clear
Figure 5.1. Correspondence between the deuterium spectrum and the deuterium satellites on a nitrogen line in L-serine hydrate.
cut satellites should probably only be used to support con-
cclusions arrived at by other methods.

Deuterium spectra are more difficult to analyse than nitro-
gen spectra because there are usually more inequivalent
sites and only $V^+$ and $V^-$ transitions are observed. Also
since the ratio of linewidth to the range of the spectrum
is much smaller for deuterium there is a much higher inci-
dence of overlapping of lines.

The comparison of a deuterium spectrum taken in zero
field with one taken in a small DC magnetic field ($\frac{1}{2}$-6
gauss) is very useful in grouping the lines. Besides en-
abling identification of $V^+$'s and $V^-$'s the magnetically
perturbed spectrum permits, in favourable instances, a
pairing of lines which undergo the same degree of assym-
metric broadening since $V^+$, $V^-$ pairs which are close in
frequency are shifted more than pairs which are further
apart. If - as in L- alanine - a series of alternating $V^+$
and $V^-$ lines beginning at one end of the spectrum is found,
then adjacent $V^+$ and $V^-$'s belong to the same deuteron.

Just as in nitrogen resonance, deuterons from particular
sites give predictable lines. Deuterons covalently bonded
to oxygen have quadrupole lines of narrower linewidth than
those covalently bonded to nitrogen. Also oxygen deuterium
lines generally occur at higher frequencies than nitrogen
deuterium lines. In table X.2 some of the systematics of
Deuterium spectra are listed.
As mentioned above, deuterium satellites provide a conclusive assignment of nitrogen deuteriums. Unfortunately, due to the contact of the deuterium levels with the proton dipolar spin bath, double irradiation is ineffective in assigning deuterium lines. The assignment of pairs of lines in fine structure as discussed in chapter VII is a risky process since it cannot be checked. A comprehensive collection of quadrupole data along with the assignments to nitrogen and deuterium sites is listed in appendices I and II.

<table>
<thead>
<tr>
<th>site</th>
<th>range in $e^2qQ$ KHz</th>
<th>$\eta$ range</th>
<th>features</th>
</tr>
</thead>
<tbody>
<tr>
<td>amide group $ND_2$</td>
<td>195 to 207</td>
<td>0.12 to 0.17</td>
<td>fine structure</td>
</tr>
<tr>
<td>$D_2O$ water of hydration</td>
<td>210 to 250</td>
<td>0.08 to 0.16</td>
<td>fine structure</td>
</tr>
<tr>
<td>$N^+D_3$</td>
<td>140 to 195</td>
<td>0.02 to 0.08</td>
<td>overlapping</td>
</tr>
<tr>
<td>tetrahedral $N^+D_2$</td>
<td>124 to 140, 165 to 195</td>
<td>0.03 to 0.12</td>
<td>frequent</td>
</tr>
<tr>
<td>$OD$</td>
<td>160 to 250</td>
<td>0.1 to 0.17</td>
<td></td>
</tr>
</tbody>
</table>
Chapter XI. Assignment of the Nitrogen Quadrupole Spectrum in Imidazole.

The molecule imidazole is of interest to biologists for its role in the conduction of electric charge through the hydrogen bridge between two adjacent nitrogens in different molecules in the crystal (42) and for its function as a preferred binding site for metal ions (43). There have been two attempts to calculate the electric field gradient tensor at the nitrogen sites in imidazole using ab initio molecular wave functions (44, 45). These calculations have been compared with the solid state NQR data of Koo and Hseih (46) who claim to have unambiguously assigned the two sets of nitrogen NQR frequencies to the correct sites in the imidazole molecule. In two publications by members of our group (47, 48), the opposite assignment was made. To try to resolve this controversy it was decided to make a comprehensive study of the assignment of the nitrogen lines in imidazole.

Imidazole has the chemical formula:

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{N(1)} \\
\text{C} \\
\text{H} \\
\end{array}
\]

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{N(2)} \\
\text{C} \\
\text{H} \\
\end{array}
\]

and the nitrogen quadrupole spectrum yields two sets of lines Sa and Sb as listed above. Koo and Hseih have assigned Sb to N(1) and Sa to N(2). The logic behind their choice was their observation of solid effect nitrogen-deuterium transitions at the frequencies \( \nu_{eN} + \nu_{eD}, \nu_{eN} + \nu_{-D} \) on the line of the Su nitrogen in a deuterium enriched sample of
imidazole. By using very high r.f. powers they produced a spectrum with lines at 131, 143.5, and 264.5 KHz from the Sb nitrogen \( \nu_0 \) line at 210.5 KHz. They interpret the absorptions at 341.5 and 354 KHz as deuterium \( \nu^- \) and \( \nu^+ \) satellites and the absorption at 375 KHz as a double satellite at \( \nu_0 + \nu^- + \nu_{PH} \).

The Koo and Hseih interpretation not only appears dubious from the evidence they have presented but it is also inconsistent with data obtained in our laboratory. Firstly it has been demonstrated conclusively that when an NH site is changed to an ND site there is an isotope shift in the nitrogen quadrupole frequencies. In the case at hand the nitrogen \( \nu_0 \) line of Sb is shifted down to 204.5 from 210.5 KHz so that the frequencies Koo and Hseih give as the deuterium lines should be increased by 6 KHz. The pure deuterium quadrupole spectrum of imidazole has been run in this laboratory and found to consist of a \( \nu^+ \) at 121.25 KHz and a \( \nu^- \) at 107.25 KHz. This would give deuterium satellites at 311.5 and 325.7 KHz in contradiction to those found by Koo and Hseih. The frequency region above the nitrogen \( \nu_0 \) was examined closely in our laboratory but with our limit of available r.f. power no deuterium satellites could be seen. However, since Koo and Hseih clearly were not measuring deuterium satellites, their case for the assignment of the nitrogen lines is invalid.

Edmonds and Speight (47) and Edmonds and Summers (48) have assigned Sa to N(1) and Sb to N(2). The evidence for this choice came from the systematics of other nitrogen
spectra and the fact the proton satellites on Sa were larger than those on Sb. Although the latter evidence does support this assignment in this case it is dangerous to put too much weight on proton satellites because one nitrogen is hydrogen-bonded and the other covalently bonded to a proton.

To pursue this problem of assignment another stage a selection of compounds similar in structure to imidazole were studied:

In table XI.1 those quadrupole lines with frequencies similar to the Sa and Sb sites of imidazole have been labelled Sa and Sb. The N$^+H_3$ sites have been labelled Sc and the N$^+H_4$ sites Sd.
<table>
<thead>
<tr>
<th>Compound</th>
<th>site</th>
<th>$e^2qQ$</th>
<th>$\eta$</th>
<th>isotopic shift in $e^2qQ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>L- histidine (monoclinic)</td>
<td>Sa</td>
<td>1437</td>
<td>0.915</td>
<td>+20</td>
</tr>
<tr>
<td></td>
<td>Sb</td>
<td>3362</td>
<td>0.131</td>
<td>+12</td>
</tr>
<tr>
<td></td>
<td>Sc</td>
<td>1305</td>
<td>0.143</td>
<td>-19</td>
</tr>
<tr>
<td>D-L-histidine</td>
<td>Sa</td>
<td>1441.2</td>
<td>0.952</td>
<td>+29</td>
</tr>
<tr>
<td></td>
<td>Sb</td>
<td>3088</td>
<td>0.207</td>
<td>+30</td>
</tr>
<tr>
<td></td>
<td>Sc</td>
<td>1246</td>
<td>0.425</td>
<td>-25</td>
</tr>
<tr>
<td>L- histidine HCl hydrate</td>
<td>Sa</td>
<td>1293</td>
<td>0.974</td>
<td>+11</td>
</tr>
<tr>
<td></td>
<td>Sb</td>
<td>1256</td>
<td>0.357</td>
<td>-30</td>
</tr>
<tr>
<td></td>
<td>Sd</td>
<td>1465</td>
<td>0.300</td>
<td>+2</td>
</tr>
<tr>
<td>Urocanic acid</td>
<td>Sa</td>
<td>1511.7</td>
<td>0.748</td>
<td>-1.7</td>
</tr>
<tr>
<td></td>
<td>Sd</td>
<td>1448</td>
<td>0.348</td>
<td>-7</td>
</tr>
</tbody>
</table>

In L and DL histidine the Sc site is clearly the N(3) nitrogen since its $e^2qQ$, $\eta$ and isotope shift are very typical of $NH_3$'s. The Sa and Sb lines, which represent the N(2) and N(1) sites, have very similar frequencies to the imidazole lines. The difference between DL or L-histidine and L-histidine HCl hydrate is that the N(2) site is replaced by an N(4) site, so the line in DL or L-histidine which belonged to the N(2) site should not be present in L-histidine HCl hydrate. The Sb line of DL and L-histidine is not present in the HCl form supporting the assignment where the Sa site in imidazole belongs to the N(1) and therefore the Sb site to N(2). Furthermore in Urocanic acid the N(1) site has quadrupole lines in the region Sa and the quadrupole frequencies for its N(4) are similar to those in L-histidine HCl hydrate.

The above data shows that there is a considerable amount of regularity in the NQR frequencies of nitrogens in the types of environments found in imidazole and this regularity points to the assignment of Sa to N(1) and Sb to N(2). It is hoped that this work will end the controversy about the assignment of $^{14}N$ NQR lines in imidazole.
Chapter XII. A Deuterium Quadrupole Resonance Study of Hydrogen Bonding in Amino Acids.

When a hydrogen atom is covalently bonded to a strongly electronegative site (e.g. O, N, S) the unit contains a net electric dipole moment which enables it to link with another electronegative atom in an association called hydrogen bonding. Although the energy required to break this association (~5 Kcal/mole) is very weak compared to that required to break a covalent bond (~100 Kcal/mole), hydrogen bonding plays a major role in the structure of molecular crystals. It is well known that hydrogen bonds are fundamental to the structure and function of proteins and nucleic acids and because they are weak enough to be made and broken at room temperature they can be very important in biological processes.

In molecular crystals where there is no specific intermolecular bonding, the distances of closest approach between two atoms is nearly a constant for all the crystalline compounds they are found in. From these distances, characteristic packing radii called the Van der Waals radii have been tabulated for each atom. A hydrogen bond can be said to exist if a proton is closer to two atoms than the sum of the appropriate Van der Waals radii. It is customary to represent the hydrogen bond with the schematic A-H...B. The atom A, covalently bonded to H, is called the donor atom and B is called the acceptor atom.

Because of its importance to biology, a great deal of research effort has been expended on the hydrogen bond. This research has progressed along four different lines:
The presence of hydrogen bonding between molecules in a compound is reflected in its physical properties. For example, the effective molecular weight is larger than the formula weight and the melting and boiling points and the latent heats are greater in hydrogen bonded systems than in similar non-hydrogen bonded systems. The collection of data of this nature is reviewed in chapter 2 of reference (49). Recent research on the thermodynamics of hydrogen bonding is presented in reference (50).

From crystallographic studies a great deal of data has been amassed on hydrogen bond lengths, angles, and statistics (50). Because x-ray diffraction techniques depend on electron density they can give accurate positions for the heavier atoms but are less reliable on hydrogen positions so before the time of neutron diffraction methods, hydrogen bonds were usually characterised by the A...B distances. But, because the neutron scattering cross-sections of hydrogen and deuterium are of the same order as those for the heavier atoms, neutron diffraction studies enable a relatively precise definition of hydrogen bond dimensions. Although in the absence of other considerations hydrogen bonds tend to be linear, in molecular crystals quite large angular deviations may be found. For example, in O-H...O bonds the range of angular deviation from linearity has been found to vary monotonically from zero for very short O...O distances (2.4 angstroms) to 25° or more for long O...O distances (3.3 angstroms). Distributions of A...B bond lengths which have been tabulated for various types of
hydrogen bonds (49, 50), indicate that the proton is always well inside the electronic clouds of the A and B atoms.

The theory of hydrogen bonding, reviewed by Bratoz (51), has a long way to go before all the experimental details can be accounted for. Simple electrostatic treatments which consider A, B, and H as charge distributions unperturbed by being close to each other predict bond energies in the right region but fail to explain either dielectric behaviour or the intensity of infrared spectra. Several more sophisticated approaches have included the effects of charge transfer from one atom to the other and repulsion due to the proximity of like charge. The most comprehensive approach is to calculate a self-consistent field molecular orbital treating A-H...B as a single unit. This method has had varied success in a number of applications (50).

Infrared vibrational spectroscopy has been by far the most popular spectroscopic technique to be applied to the study of hydrogen bonding. It has a high sensitivity, it can be applied to molecules in the gas, liquid or solid phases and it is particularly applicable to the study of low concentrations of hydrogen bonded molecules in inert solvents. From an infrared spectrum of a compound it is possible to extract not only which sites contain hydrogen bonds but also some measure of the strength of the hydrogen bond and the shape of the potential well governing the position of the proton in the bond. A monotonic relationship has been shown experimentally (50) to exist between the change in enthalpy and change in A-H stretching frequency on hydrogen bonding. Also, a correlation (51, 52)
has been made between the deuterium quadrupole constant $e^2qQ$ and the square of the A-H stretching frequency. An advantage of infrared spectroscopy, common to all spectroscopic techniques, over the measurement of physical properties is that intramolecular hydrogen bonding can be detected.

Another spectroscopic technique used extensively in the study of hydrogen bonding is proton magnetic resonance (53). In high resolution magnetic resonance, which can be applied to pure liquids or solutions, hydrogen bonding causes a downfield shift in the proton magnetic resonance lines. Because, due to rapid proton exchange, the net chemical shift is a weighted average over all proton sites, the concentration and temperature dependence of the chemical shift can, in favorable cases, yield equilibrium constants and thermodynamic functions of hydrogen bonded systems. Proton magnetic resonance lineshape measurements in solids, liquids, or gases may be used to examine the kinetic aspects of the proton in the hydrogen bond. $^1$C, $^2$H, $^3$N and $^5$N magnetic resonance have also been employed in the study of hydrogen bonding (49).

There are several instances in the literature where quadrupole resonance parameters have been correlated with other parameters. T. Chiha (54, 15) has measured deuterium quadrupole constants in a considerable number of O-D...O bonds using deuterium magnetic resonance and single crystals. He has demonstrated that the value of $e^2qQ$ for long O...O distances ($R(O...O)$) is independent of $R(O...O)$ and has the
XII.5

magnitude of $e^2qQ$ in a non-hydrogen bonded OD. The effects of hydrogen bonding in O-D...O bonds begin at an $R(O...O)$ of about 3.3 angstroms and as $R(O...O)$ gets shorter $e^2qQ$ is found to decrease asymptotically toward zero at an $R(O...O)$ of about 2.4 angstroms.

Of the empirical correlations which have been made between deuterium $e^2qQ$'s and other spectroscopic or crystallographic parameters in O-H...O bonds, one of the most convincing has been between $e^2qQ$ and the inverse cube of the $R(D...O)$ distance. Chiba has found a relationship of the form:

$$e^2qQ = 310 - 372/R(U...O)^3 \text{ (kHz)}$$  \hspace{1cm} (XII.1)

There appears to be no direct theoretical justification for this empirical relation, in fact it has been calculated (55) that for a fixed OD distance $e^2qQ$ should be insensitive to changes in O...O distance but that, on the other hand, $e^2qQ$ should be very sensitive to small changes in the OD distance. However, plots of $e^2qQ$ versus the inverse cube of the OD distance show a lot of scatter (56) but this may be partly due to error in the OD distances and the inverse cube may be the wrong functional representation.

Salem (51) has predicted theoretically and Blinc and Hadzi (52) have demonstrated experimentally that a linear correlation exists between the deuterium $e^2qQ$ and the square of the OH stretching frequency in a hydrogen bond. This is because both quantities are proportional to the force constant of the bond. Renne' and Depireux (14) have demonstrated a roughly linear relation between deuterium $e^2qQ$ and the force constant in O-D bonds.

An advantage of using deuterium $e^2qQ$'s rather than infrared
vibrational data for hydrogen-bonding correlations is that while $\omega^2 q_4$'s vary over the whole range of strengths of bonds, infrared stretching frequencies are nearly constant for very strong bonds. In addition, infrared stretching frequencies change by a factor of only 2 to 3 in the range of hydrogen bonding while deuterium $\omega^2 q_4$'s can change by a factor of 5 or more in the same range.

Due to the ease of obtaining deuterium spectra with the laboratory frame double resonance apparatus in our laboratory, a wealth of quadrupole data has been accumulated on $\text{O} \cdots \text{H} \cdots \text{O}$ bonds and $\text{N} \cdots \text{H} \cdots \text{O}$ bonds (see appendix II). The recent emergence in the literature of a series of neutron diffraction structures of crystalline amino acids by a research group at Brookhaven has provided the opportunity to look for correlations between this data and the crystal structures.

Since all the neutron diffraction studies are on undeuterated compounds and the quadrupole data comes from deuterated compounds it is important to find out what happens to the structure when a deuteron is substituted for a proton. The isotope shifts in the nitrogen quadrupole spectra of deuterated compounds have been small and regular indicating no radical change occurs to the structure on deuteration.

When a proton is replaced by a deuteron, two not necessarily independent effects occur (49): the lower zero point energy of the deuteron causes it to move to a different equilibrium position in the asymmetric potential well and the dipole moment of the $\text{A} \cdots \text{H}$ bond is different from that of an $\text{A} \cdots \text{H}$ bond. These factors usually result in a slight expansion in
OH bond length on deuteration (39). Because the bond length changes are very small (∼0.03 angstroms (39)), it is believed that structures of the undeuterated compounds can justifiably be used in correlations with quadrupole parameters in deuterated compounds.

A plot of deuteron $e^2qQ$ versus the inverse cube of $R(\cdot\cdot\cdot O)$ for the new data on O-D...O bonds is shown in figure XII.1. Since most of the compounds contained only one OD site, assignment of the appropriate $R(\cdot\cdot\cdot O)$ to an $e^2qQ$ presented no problem. In waters of hydration with fine structure, to eliminate the uncertainty in assignment the average $e^2qQ$ was matched with the average value of $1/R(\cdot\cdot\cdot O)^3$ for the two sites. In L-glutamic acid which contains an C-D...O and an O-D...Cl bond, since one $e^2qQ, 1/R(\cdot\cdot\cdot O)^3$ pair fitted on the line of correlation and the other was well off the line, the latter was assigned to the O-D...Cl site. A least-squares analysis of the O-D...O data gave a relation of the form:

$$e^2qQ = 328 - 643/R(\cdot\cdot\cdot O)^3 \text{ KHz}$$

(XII.2)

If this is extrapolated to infinite $R(\cdot\cdot\cdot O)$, i.e. no hydrogen bonding, an $e^2qQ$ of 328 KHz is obtained. This may be compared with the experimental values of 315±7, 310±3, 314±1.5 and 318.6±2.4 in the free water molecule (57) and 320 in LiOD (58) which does not form hydrogen bonds. Equation XII.2 agrees substantially with Equation XII.1 which was obtained with considerably more data.

Chiba (59) has predicted the existence of a correlation between deuterium $e^2qQ$ and bond distances in $\Lambda^4$-D...O bonds but he had insufficient data to check it. In appendix II there is enough quadrupole data on $\Lambda^4$-D...O bonds to look
Figure XII.1. A plot of deuterium e°Q against \( \frac{1}{R^3} \) in O-O bonds. The number and letter beside each data point refer to the assignments in Appendix II. The line represents equation XII.2.
for correlations. Since there are usually a number of N-D sites in a compound the assignment of each quadrupole frequency to a bond distance is more difficult than in the O-D case. The procedure used was to assume that $e^2qQ$ increases with increasing $R(\text{N}...\text{O})$ (e.g., in an ND$_3$ site the smallest $e^2qQ$ was assigned to the smallest $R(\text{N}...\text{O})$ and the largest $e^2qQ$ to the largest $R(\text{N}...\text{O})$). In L-glutamic acid, which has two N$^+$D...Cl sites and one N$^+$D...O site, the value of $e^2qQ$ which came closest to fitting on the $e^2qQ$ vs $1/R(\text{N}...\text{O})^3$ curve was associated with the N$^+$D...O bond.

Three possible correlations were examined with the N$^+$D...O data: $e^2qQ$ versus $1/R(\text{N}...\text{H})^3$, $1/R(\text{N}...\text{O})^3$, and $1/R(\text{N}...\text{O})^3$. It turns out that N-H distances are not suited for correlations for two reasons; they change by only a small amount in the range of hydrogen bond strengths and because $R(\text{N}...\text{H})$ is short compared to other distances e.g. $R(\text{N}...\text{O})$, the uncertainty in the hydrogen position gives N-H distances a proportionately higher percentage error. The $e^2qQ$ versus $1/R(\text{N}...\text{H})^3$ curve suggested some correlation but there was a considerable amount of scatter in the points. The plot representing $e^2qQ$ versus $1/R(\text{N}...\text{O})^3$ showed practically no correlation.

The most promising correlation is that between $1/R(\text{N}...\text{O})^3$ and $e^2qQ$ illustrated in figure XII.2. A least-squares analysis of this plot yielded the equation:

$$e^2qQ = 252 - 572/R(\text{H}...\text{O})^3 \text{ kHz} \quad (\text{XII.3})$$

It is interesting that the coefficient of $1/R(\text{H}...\text{O})^3$ is the same as the one obtained by Chiba in his correlations on O-D...O bonds so this coefficient apparently depends on
Figure XII. 2 A plot of deuterium e'q'q against 1/R(D⋯O)² in N⋯O⋯O bonds. The assignments of the data points are given in Appendix II. The line represents equation XII.3. The points AO are for ammonium oxalate monohydrate (59).
the acceptor atom alone.

Recently there has appeared in the literature (60) a theoretical calculation on the deuteron $e^2qQ$ in the ammonium ($N^+D_4$) ion. They find that the N-D distance and the orbital parameters which lead to a minimum in energy for the free $N^+D_4$ ion give a deuteron $e^2qQ$ of about 250 KHz. This compares favourably with our predicted value of 252 KHz for a non-hydrogen bonded N-D. It is difficult to see how this could be checked experimentally.

A criticism of the above treatment is the fact equation XII.3 was practically assumed in the assignment of sites so that, already, for each individual compound there is a monotonic decrease in $e^2qQ$ with increasing $1/R(H...O)^3$. To check this the average $e^2qQ$ and average $1/R(H...O)^3$ for all the sites in each molecule were plotted against each other. The result was a smaller range of points than in figure XII.2 but the points were distributed fairly closely about the line given by equation XII.3.

Goren (56) has calculated that the deuterium $e^2qQ$ in O-D...O bonds is relatively insensitive to changes in the O-D...O angle. This can now be checked for both O-D...O and N-D...O bonds. In the O-D...O case hydrogen bond angular deviations from linearity range from 3 to 20 degrees but there is no correspondence between inability to fit equation XII.3 and bond angle. The range of angular deviation is considerably larger - from 7 to 67 degrees - in N-D...O bonds. But again there is no relation between the distance from the fitted line and the H-bond angle; indeed the points representing the three largest bond angles are right on the line!

A further remarkable property of the quadrupole data is
that it appears to be independent of the hybridization of the acceptor oxygen atom. The four types of oxygen atoms which act as acceptors - negatively charged carbonyls, neutral carbonyls, hydroxyl groups, and waters of hydration - yield $e^2qQ$'s which fit equations XII.2 or XII.3 equally well. In the O-D...O data there are several types of oxygen donors but figure XII.1 gives no indication of any corresponding difference in the $e^2qQ$, $1/R(H...O)^3$ relation.

The five $e^2qQ$'s from N-D...Cl bonds are plotted against $1/R(H...Cl)^3$ in figure XII.3. There are clearly not enough points to permit a conclusive statistical analysis but a least-squares fit gives the following linear correlation:

$$e^2qQ = 239 - 728/R(H...Cl)^3 \text{ KHz} \quad (XII.4)$$

It is worthy of notice that the value of the intercept, 239, - the $e^2qQ$ of an isolated N-D bond - is not very different from that predicted in the N-D...O correlations, 253. Unfortunately there is not enough data from O-D...Cl sites to obtain a fitted line but one should expect a line of the form:

$$e^2qQ = 320 - 730/R(H...Cl)^3 \text{ KHz}$$

The two points obtained so far fall below this line.

Chiba (59) has measured the deuterium quadrupole spectrum of ammonium oxalate monohydrate using deuterium magnetic resonance on a single crystal sample. When his data is plotted on figure XII.2 three of the sites fit fairly well but the fourth is a considerable distance from the line. Because Chiba used a single crystal he was able to obtain field gradient principal axes and thus positively assign each of the $e^2qQ$'s to deuteron sites. On consultation with
Figure XII.3. A plot of deuterium e\(^2\)g against \(1/\hbar (D-\cdots X)^3\) in N-D-\cdots Cs bonds. The assignments of the data points are in Appendix II. The line represents equation XII.4.
the neutron diffraction of ammonium oxalate monohydrate (61),
it is, at first glance, disturbing to find out that the
increasing $e^2qQ$ with increasing $R(H...O)$ rule does not hold
here but, however, the $e^2qQ$'s differ very little in magni­
tude so that an error in assignment would make little diff­
ference to the plot. The point representing the average $e^2qQ$
and the average $1/R(H...O)^3$ fits closely to the line.

It is unfortunate that neutron diffraction structures have
not yet been produced for the amides, since the quadrupole
spectra have been obtained for several of them. If $N-H...O$
bonds of amides follow the trend observed in $O-H...O$,
$N^+H...O$, and $N^+H...Cl$'s a relationship of the form:

$$e^2qQ = 282 - 572/R(H...O)^3$$  \(\text{XII.5}\)

should be expected. 282 is the value of $e^2qQ$ in the free
ammonia molecule (59). The only values of $e^2qQ$ and $1/R(H...O)^3$
available to test this relation are from acetamide. Since
x-ray studies are known to predict $N-H$ distances smaller
than those from neutron diffraction studies (61), the $N-H$
distances were chosen each to be 1 angstrom rather than .93
and .96 angstroms but the $N...O$ distances and the hydrogen
bond angles were taken from the x-ray structure (41).

With these distances, the point representing the average
acetamide $N-D$ $e^2qQ$ and the average $1/R(H...O)^3$ is fairly
close to the line defined by equation XII.5.
Chapter XIII. An NQR Study of the Water Molecules.

Because water is the primary constituent of living matter and the most abundant compound on the earth there is a great deal of interest in the study of the molecular associations in which it participates. This chapter presents an account of an experimental attempt to find out what can be obtained from a nuclear quadrupole resonance analysis of the water molecule in a variety of different environments.

The most extensive NQR study has been carried out on ice Ih, the natural crystalline form of water. In ice Ih the water molecules are loosely packed in a hexagonal structure where each molecule is bonded to four neighbours. Each oxygen is bonded to four hydrogens, two of the bonds being covalent and the other two being hydrogen bonds. This leads to a structural disorder since there are six equivalent ways of arranging two covalent and two hydrogen bonds among four bonds. At nitrogen temperature the hydrogen disorder in ice Ih is believed to be static (63). The structures of H_2O and D_2O ice Ih have only very slight differences in bond angles and bond lengths (49).

Unfortunately ice contains no inexchangeable hydrogens so deuterium quadrupole resonance has to be carried out in a partially deuterated sample. In figure XIII.1 the NQR spectra for a range of concentrations of D_2O in H_2O are illustrated. For very low D_2O concentrations a single pair of broad lines are obtained but the more concentrated samples give spectra with doublets for V- and V+ and the centres of these doublets are slightly shifted from the centres of the
Figure XIII 1 Quadrupole spectra of ice Ih for several D_{2}O concentrations.
XIII.2

lines in the dilute samples.

It has been well proven (chapter VIII, 62) that in a D₂O molecule where the deuterons have nearly degenerate levels, the presence of an interaction between the two deuterons results in a fine structure in the quadrupole resonance spectrum. In pure D₂O ice Ih the electric field gradients at the two deuteron sites should be expected to be very similar except for small differences caused by slight changes in the bond lengths due to the static structural disorder. If the two deuteron sites are assumed to be degenerate the fine structure pattern becomes particularly simple. The separation between the two main \( \nu^+ \) lines is equal to twice the value of the matrix element \( D(0A) \) between the levels \( \nu^0 \) and \( \nu^A \) in the composite system and similarly the separation of the two main \( \nu^- \) lines is twice the value of \( D(0B) \) (using the notation of chapter VIII).

The eigenfunctions for the upper and lower levels in a degenerate pair are now equal mixtures of the two quadrupole states in the composite system i.e. \( |\nu^0 A\rangle = \frac{1}{\sqrt{2}} (|\nu^0 A\rangle + |\nu^A A\rangle) \), \( |\nu^A A\rangle = \frac{1}{\sqrt{2}} (|\nu^0 A\rangle - |\nu^A A\rangle) \) etc. Then all the subsidiary lines for a particular transition (\( \nu^+ \) or \( \nu^- \)) should have the same intensity and since the sum of intensities of the four subsidiary lines in one fine structure pattern is equal to the intensity of one of the main lines (chapter VIII), each subsidiary line should have one-quarter the intensity of a main line. The positions of the subsidiary lines are determined by the values of the matrix elements.

If it is assumed that in ice the interaction between a deuteron and other deuterons and protons in neighbouring
molecules can be neglected, a quadrupole spectrum should contain two types of lines, those from HDO molecules and those from D₂O molecules. In a sample with a low concentration of D₂O the HDO spectrum should predominate and in a highly concentrated sample the D₂O spectrum should account for most of the absorption. A computer curve fitting analysis was carried out to test these predictions.

If the ratio of the number of D₂O molecules to the total number of molecules in the sample is D, then, assuming it is equally likely that any given site is occupied by a deuteron or a proton, in the D₂O/H₂O mixture the probability of finding two deuterons in one molecule is D², that of finding two protons is (1-D)², and that of finding one proton and one deuteron is D(1-D)+(1-D)D = 2D(1-D). Then a sample with D = 0.09 has about 20 times as many HDO molecules as D₂O molecules and the observed quadrupole spectrum is from the HDO molecule. In a computer fit of a sample with D = 0.089, the HDO spectrum was reproduced by two Gaussians: the V⁻ at 154.0 and the V⁺ at 166.9 KHz and both of linewidth 2.6 KHz.

A five line pattern was chosen to represent the D₂O spectrum. Because the linewidths involved are relatively large and the matrix elements are expected to be similar it seems reasonable to assume the matrix elements are equal. Then the two inner subsidiary lines coincide at the centres of the fine structure patterns and they have a combined intensity of one-half that of a main line. The positions of the two main lines for both V⁺ and V⁻ were found by computer fitting and the outer subsidiary lines were positioned as...
XIII.4

far from the main lines as the main lines were from the
centre of each pattern. The outer subsidiary lines were
each given an intensity one-quarter that of the main line.
Using the ice Ih spectrum from a mixture with $D = 0.787$ the
optimum positions for the five line fine structure patterns
were found in a least-squares fit, varying the line posi­
tions, linewidths and amplitudes of the $\nu^+$ and $\nu^-$ D$_2$O spec­
tra and the relative amplitude of the superimposed HDO
spectrum. The best fit was obtained with the main $\nu^-$ lines
at 152.9, 155.3 KHz, the main $\nu^+$ lines at 164.8, 167.4 KHz
and a D$_2$O linewidth of 2.2 KHz. The fitted HDO and D$_2$O com­
ponents for the $D = 0.787$ ice Ih spectrum are drawn in
figure XIII.2.

The D$_2$O fit was tried with both Gaussian and Lorentzian
lineshapes but the Gaussian gave the smaller least square
error. This suggests that the D$_2$O lines are inhomogeneously
broadened and since the optimum linewidth was around 2.2
KHz and D$_2$O lines in organic hydrates are usually about 0.6
to 0.8 KHz this may be the case. The main causes of inho­
genous broadening in ice Ih would be expected from the
static structural disorder and the perturbations from hydro­
gens in neighbouring molecules in the crystal. If the
broadening were entirely due to the structural disorder the
observed linewidth could occur from a deviation in H...O
bond lengths of about one-hundredth of an angstrom. Infrared
studies on ice Ih have predicted similar deviations in bond
lengths (40).

The computed ice Ih D$_2$O lines yield an $e^2qQ$ of 213.5(1)
KHz and an $\eta$ of 0.112(2). These compare favourably with the
Figure XIII.2. The HDO and D2O components used in the curve fits to the ice Ih data. The fit for the case where D = 0.787 is shown.
currently accepted values of 213.2\,(8) kHz and 0.100\,(2)
obtained from an NMR analysis at -10°c (63). The fact that
our values were obtained from a more sophisticated analysis
and with lines of width 2.2 kHz whereas the NMR study
found linewidths of order 3.5 kHz may be significant.

Assuming degeneracy of the quadrupole levels, the fre­
quencies of the two main lines of the $\nu^+$ and $\nu^-$ patterns in
the computed $D_2O$ spectrum yield $D(\nu A)$ equal to 1.3 kHz and
$D(\nu B)$ equal to 1.2 kHz. The fact these values are slightly
higher than expected from OD bonds of 1.01 angstroms and a
DOD angle of 105° suggests the sets of levels may not be
truly degenerate. However, these are the two most nearly
degenerate sets of $\nu^+$ and $\nu^-$ lines yet observed in this lab­
oratory. The fact the HDO lines are very little broader than
one of the main $D_2O$ lines and that only one "HD" line exists
for each pair of $D_2O$ lines strongly supports the idea that
the $D_2O$ quadrupole levels are very nearly degenerate. The
$\nu^-$ "HD" line is shifted about 0.1 kHz down from the centre
of the $D_2O$ $\nu^-$'s and the $\nu^+$ "HD" is about 0.8 kHz higher in
frequency than the centre of the $D_2O$ $\nu^+$ pattern hence
agreeing in direction but not in magnitude with predicted
HD shifts (chapter IX) of -0.6 kHz for $\nu^-$ and +0.3 kHz for $\nu^+$.

By adding the computed HDO lines to the computed $D_2O$
lines and adjusting their relative contributions, curve fits
were obtained for the ice Ih data all through the concen­
tration range from $D = 0.09$ to $D = 0.91$. Since with the
laboratory frame double resonance method the sensitivity to
$\nu^+$ and to $\nu^-$ transitions may not be the same for all con­
centrations, the amplitudes of the $\nu^+$ and $\nu^-$ lines were
varied separately but the HDO/D₂O ratio was maintained constant for both lines. It was comforting to find out that the fitted HDO/D₂O ratio was not particularly sensitive to small changes in line frequencies or widths (provided differences in included area are accounted for). To account for the fact a D₂O molecule gives three times the absorption that one deuteron would give and the fact D₂O lines have narrower widths than HDO lines, the fitted HDO/D₂O ratios were multiplied by 3 x 2.2 KHz/2.6 KHz (using the property that the area underneath a Gaussian is proportional to the product of its linewidth and amplitude). As a function of D, the value of the best fit HDO/D₂O ratio is plotted along with the actual HDO/D₂O ratio in figure XIII.3.

The shapes of the two curves in figure XIII.3 are similar, but, since the sensitivity of the experiment depends on the proximity of protons it is not surprising that the two curves do not coincide. In fact, throughout the concentration range between D = 0.5 and D = 0.8 the apparatus appears to be approximately twice as sensitive to deuterium in HDO molecules as in D₂O molecules.

A preliminary, and as yet incomplete, deuterium quadrupole study on another form of ice, known as ice II, has been launched in collaboration with a physicist at Kings College, London - Dr. W. Sherman. Ice II is a more dense form of ice (density 1.17 g/cm³) which does not have the structural disorder found in ice Ih. It may be produced by maintaining 3 kilobars pressure on ice Ih at about -40°C and after
Figure XIII.3. A comparison between the actual HDO/D$_2$O ratios and those obtained from the curve fits of the ice Ih spectra.
formation it is stable under normal pressures provided it is kept at liquid nitrogen temperature. The neutron diffraction of ice II (64) predicts two inequivalent water molecules per unit cell but the hydrogen positions are not well known.

The ice II samples were prepared at Kings College by Dr. Sherman and transported to Oxford under liquid nitrogen. Three ice II deuterium spectra have been run with $D = 0.15$, 0.80 and . Unfortunately the proton $T_1$'s of the former two samples were very long (15-20 minutes) so a very long period of time was required to obtain a spectrum and the signal to noise was not very good. However the third sample had a more reasonable proton $T_1$ and gave a better spectrum (figure XIII.4). In the high $D_2O$ concentration ice II samples there are four $\nu^+$ lines and four $\nu^-$ lines. Both $\nu^+$ and $\nu^-$ are made up of two sets of doublets. In the low $D_2O$ concentration sample the upper set of doublets for both $\nu^+$ and $\nu^-$ have a much lower intensity. It is tempting to credit the lower doublets to HDO molecules and the upper doublets to $D_2O$ molecules but there is as yet insufficient data for any firm conclusions. The linewidths of the ice II lines are less than those of the ice Ih lines, consistent with the lack of structural disorder in ice II.

The $^{17}O$ spectrum has been run for both the ice Ih and ice II and a significant difference was found between the two. For ice Ih $\epsilon^2 \kappa \Omega$ and $\gamma$ were found to be $6532 \text{ KHz}$ and $0.9215$. In ice II, lines were found at $3580 \text{ KHz}$, $1900 \text{ KHz}$ and $1705 \text{ KHz}$ and there was a trace of a line at $1770 \text{ KHz}$.
Figure XIII. 4. (a) Quadrupole spectrum of ice II: V-lines.
Figure XIII.4. (b) Quadrupole spectrum of ice II: V+ lines
corresponding to the $^{17}$O$^{-}$ in ice Ih. Because the three main lines do not satisfy $V_2 + V_3 = V_1$ accurately there is some uncertainty but if they are assigned to one $^{17}$O nucleus an $e^2qQ$ and $\eta$ of 7028(40) KHz and 0.87 are obtained.

A clathrate hydrate (65) is a crystalline compound consisting of a "host" lattice of hydrogen bonded water molecules which have enclosures that can contain one or more "guest" molecules. Ordinarily the interaction between the host and guest is Van der Waals but it may also be ionic or hydrogen bonding. It would be very interesting to obtain NMR spectra from water in clathrate hydrates but unfortunately the nature of the clathrate allows freedom for re-orientation of the guest molecule and hence a means of producing a short proton $T_1$. Out of eight clathrates that have been tried only one had an acceptable proton $T_1$ - Hexamethylenetetramine Hexahydrate (HMT hydrate). In HMT hydrate a number of hydrogen bonds between the guest and the water framework prevents the guest HMT molecules from reorientating. The x-ray structure of the water framework of HMT hydrate (66) indicates that one proton of each water molecule is disordered over two positions hence a partially ordered structure exists which is somewhere intermediate between the totally disordered arrangement in ice Ih and the completely ordered case in ice II.

The deuterium quadrupole spectrum of HMT hydrate has been run in a sample containing 100% D$_2$O. The results support the predicted x-ray structure in that there appears to be one intense $V^+,V^-$ pair and two $V^+,V^-$ pairs which are about...
XIII.9

one-half as intense. The more intense pair have an $e^2Q_\eta$ of 221.3(2) and $\eta = 0.11$ and the most likely assignments for the other two $V+V-$ pairs is $e^2Q_\eta = 199.3(2)$, $\eta = 0.12$ and $e^2Q_\eta = 205.3(2)$ and $\eta = 0.12$. It is somewhat surprising that the linewidths of $D_2O$ in ice Ih and HMT hydrate are not substantially different.

L-proline hydrate is an organic hydrate in which one of the protons in the water of hydration has been predicted to have a static disorder between two positions (67). This can be investigated by $\nu QK$. There are three inequivalent sites in the $\Lambda D$ deuterium spectrum of L-proline hydrate; one site has an $e^2Q_\eta$ and $\eta$ of 132.8 kHz and 0.02 and the other two are 186.5, 0.07 and 192.5, 0.045. Using the property of $e^2Q_\eta$'s noted in chapter XII it can be seen that the water disorder has an effect on the electric field gradient at the $ND$ deuterium site which has the longer $R(D...O)$ (because $R(NH)$ is inversely related to $R(H...O)$ (68), the disordered $ND$ site is the one with the shortest $ND$ distance). In the $D_2O$ quadrupole spectrum there are four inequivalent sites so there is effectively a disorder in both deuterons of the water of hydration in L-proline hydrate. On the basis of their magnetic field dependence the quadrupole lines can be assigned to water molecules (i.e. $D_2O$ pairs), but the fine structure is not resolved well enough to permit assignment within a $D_2O$ pair so only mean $e^2Q_\eta$'s and $\eta$'s can be given for each water molecule. The two possible orientations of the $D_2O$ molecules give mean $e^2Q_\eta$'s and $\eta$'s of 236.1, 0.107 and 224.7, 0.112. In both the $ND$ disorder and $D_2O$ disorder
the two alternative spectra are of the same intensity indicating an equal probability for a given molecule to be in one state or the other.

These results, including predictions of $\alpha(D...O)$'s in the N-D...O and O-D...O bonds using equations XII.2 and XII.3 have been sent to researchers at Brookhaven National Laboratory, New York and the Institut Lave-Langevin, Grenoble who are working on the neutron diffraction structures of L-proline hydrate.

Several other molecular compounds with water have been run in the laboratory. When a solution of formamide and water is frozen the nitrogen spectrum indicates two inequivalent sites; one is identical to the pure formamide spectrum and the other is attributed to a formamide-water complex. As the concentration of water is increased the lines belonging to the formamide-water complex become more intense and the pure formamide lines get smaller. This work has been reported in N.J. Hunt's D. Phil thesis (29).

In a $^{23}$Na quadrupole resonance study of NaOH water mixtures two NaOH water molecular complexes have been distinguished. Pure NaOH gives a line at 1917 KHz, a 1:1 molecular mixture has a line at 1203 KHz and a NaOH:$^2$H$_2$O mixture gives a line at 684 KHz. The proton $T_1$ of the mixtures was found to vary considerably with concentration. A colleague, Ian Mailer, is currently researching on the topic of molecular complexes between NaOH and water.
Phenol has a helical structure with 6 molecules per unit cell (69). The deuterium quadrupole spectrum indicates three inequivalent deuteron sites but unfortunately all three $V^+$ lines are higher in frequency than any of the $V^-$ lines so it is difficult to assign $V^+$,$V^-$ pairs unambiguously. Phenol readily picks up a very small proportion of water to produce a viscous liquid at room temperature. When this mixture is cooled to nitrogen temperature the quadrupole spectrum is quite similar to that of dry phenol except that the middle line of the three $V^+$ lines and the middle line of the three $V^-$ lines are shifted down frequency by about 1 KHz while the other two lines are shifted by less than one half KHz. Then it would appear that the two middle $V^+$ and $V^-$ lines can be paired. Having made this assignment, to conform to the systematics of previous CD spectra the upper of the $V^+$ and $V^-$ lines and the lower of the $V^+$ and $V^-$ lines should be paired to each other. Then on this basis anhydrous phenol has three sites with $e^2\eta$ and $\eta$ values: 206.2,0.141; 202.3, 0.147; and 198.6,0.145 and when a small amount of water is added the three sites take on $e^2\eta$'s and $\eta$'s of 206.0,0.144; 201.2,0.154; and 199.1,0.144. The concentration of water was too small to permit resolution of the D$_2$O spectrum. When Phenol is dissolved in dioxan, a molecular complex occurs where there is only one deuteron site and it has an $e^2\eta$ of 206.6 and an $\eta$ of 0.154.

Several unsuccessful attempts have been made to observe structured water in various environments including gels, frozen ionic solutions and collagen. Very small concentrations
of gelatine in water can cause the water to form a gel at room temperature. However, at room temperature the proton $T_1$ is too short to run the gel and at nitrogen temperature the observed spectrum is similar to that obtained from pure D$_2$O indicating that the gel may not exist at nitrogen temperature. Similar results were obtained with an agar-water mixture. A large number of aqueous solutions containing various ionic compounds including NaCl, BaCl$_2$, NaCl, Li acetate, and LiCl in a range of concentrations all gave the well known HDO quadrupole spectrum at nitrogen temperature. In these samples the proton signal appeared to be made up of two factions - one with a long proton $T_1$ and the other with a short proton $T_1$ - with very little communication between the two types of protons. One explanation for this is that on freezing the samples separate into a heterogeneous mixture of a water-solute complex with a fast proton $T_1$ and pure water. On past experience it appears that spin-spin interaction cannot occur across crystallite boundaries so the two components are isolated from each other.

A number of unsuccessful attempts have been made to reduce the proton $T_1$ in collagen so that the quadrupole spectrum of the ordered water around the triple helix could be obtained. Unfortunately, there is some speculation (70) that even if the $T_1$ could be increased sufficiently, the water structure about the collagen helices might be destroyed at nitrogen temperatures.
Chapter XIV. Application of the Laboratory Frame Double Resonance Technique to Other Nuclei.

The laboratory frame double resonance apparatus in our laboratory was built originally to observe \(^1^4\)N quadrupole spectra but after about a year it was found to be ideally suited for pure quadrupole resonance in \(^2\)H and also for \(^1^7\)O. In theory our technique should be applicable to any quadrupolar nucleus which has an energy splitting below 30 MHz, an interaction with protons in the sample and appropriate \(\gamma\)’s. Indeed, when the energy splittings are a few MHz or less it could be the easiest and also one of the most sensitive ways to do quadrupole resonance. In an exploration for spectra from other quadrupolar nuclei in order to demonstrate the versatility of the laboratory frame double resonance method spectra were obtained from six different additional nuclei. Because the new nuclei were not of spin 1 like \(^1^4\)N and \(^2\)H but of spins \(3/2\), \(5/2\), and 3, to extract quadrupole parameters from the experimental data the quadrupolar Hamiltonian had to be solved for each case.

In zero magnetic field the Hamiltonian for a spin nucleus is:

\[
\mathcal{H}_Q = \frac{1}{12} e^2 q Q \left[ 3 I_z^2 - \frac{15}{4} + \frac{\eta}{\gamma} \left( I_+^2 + I_-^2 \right) \right]
\]

It is convenient to write the Hamiltonian in a representation with the magnetic base states \( |3/2\rangle, |1-1/2\rangle, |1+1/2\rangle, |1-3/2\rangle \) taken along the principal axes of the electric field gradient. The result is:

\[
\mathcal{H}_Q = \frac{e^2 q Q}{12} \begin{pmatrix}
3 & \sqrt{3} \eta & 0 & 0 \\
\sqrt{3} \eta & -3 & 0 & 0 \\
0 & 0 & -3 & \sqrt{3} \eta \\
0 & 0 & \sqrt{3} \eta & 3
\end{pmatrix}
\]
This is very simply solved to obtain two sets of doubly degenerate levels:

\[
\psi_1 = -b |\frac{3}{2}\rangle + a |\frac{1}{2}\rangle + a |\frac{3}{2}\rangle
\]

\[
\psi_2 = a |\frac{3}{2}\rangle + b |\frac{1}{2}\rangle + \alpha |\frac{3}{2}\rangle
\]

\[
\psi_3 = b |\frac{1}{2}\rangle + a |\frac{3}{2}\rangle - a |\frac{3}{2}\rangle
\]

\[
\psi_4 = a |\frac{1}{2}\rangle - b |\frac{3}{2}\rangle
\]

where

\[
a = \sqrt{3} \left(1 - \sqrt{1 + \eta/3}\right)
\]

\[
b = \frac{\eta}{\sqrt{3} (1 + \eta/3 - \sqrt{1 + \eta/3})^2}
\]

An r.f. field along one of the principal axis directions can induce transitions between the energy levels.

<table>
<thead>
<tr>
<th>Direction of r.f.</th>
<th>Transition</th>
<th>Transition</th>
<th>Energy</th>
<th>Probability</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z</td>
<td>\psi_1 ↔ \psi_2, \psi_3 ↔ \psi_4</td>
<td>4a^2b^2</td>
<td>e^2qQ/2(1 + \eta/3)^{1/2}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X,Y</td>
<td>\psi_1 ↔ \psi_3, \psi_2 ↔ \psi_4</td>
<td>\frac{1}{2}(a^2+b^2-2\sqrt{3}ab)</td>
<td>e^2qQ/2(1 + \eta/3)^{1/2}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Then in zero field there are only two energy levels and one transition frequency. This is unfortunate because it means that for spin \( \frac{1}{2} \) nuclei extra measures have to be taken to obtain \( e^2qQ \) and \( \eta \) independently from the quadrupole data.

In favourable cases the symmetry of the bonding configuration of the nucleus dictates the value of the asymmetry parameter (e.g. if there is axial symmetry \( \eta \) must be close to zero). Then it is a simple matter to calculate \( e^2qQ \) from the transition frequency. If a single crystal is used, the perturbation of the quadrupole lines when a weak magnetic field is applied enables \( \eta \) to be evaluated (71) and in a powder sample, if the r.f. field is aligned parallel to an applied magnetic field, a value for \( \eta \) can be derived from
the structure which appears on the resonance line (72).

The transition frequencies and linewidths from the spin $3/2$ nuclei which were run successfully are listed in table XIV.1. No attempt was made to calculate the asymmetry parameters since the main aim was to demonstrate that quadrupole resonance could be observed in these nuclei with the laboratory frame double resonance method. Sodium 23 and Boron 11 were detected with very high sensitivity - a consequence of their relatively high gyromagnetic ratios. Some effort was spent in looking for a line from potassium 41 in potassium dihydrogen phosphate. Although its position was known from the frequency of the $^{39}K$ line and the ratio of quadrupole moments of $^{39}K$ and $^{41}K$, no trace of it could be found. This may not be surprising since $^{41}K$ is only 0.9% abundant and has a low gyromagnetic ratio. In the boron glasses lines were observed from both $^9B$ and $^{10}B$. The solving of the boron 10 spectrum will be discussed later.

**TABLE XIV.1**

Quadrupole resonance in spin $3/2$ nuclei

<table>
<thead>
<tr>
<th>nucleus</th>
<th>compound</th>
<th>transition frequency</th>
<th>linewidth KHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{23}Na$</td>
<td>NaOH</td>
<td>1917</td>
<td>13</td>
</tr>
<tr>
<td>$^{25}Na$</td>
<td>NaOH.H$_2$O</td>
<td>1203(2)</td>
<td>20</td>
</tr>
<tr>
<td>$^{23}Na$</td>
<td>NaOH.4H$_2$O</td>
<td>684(2)</td>
<td>25</td>
</tr>
<tr>
<td>$^{39}K$</td>
<td>KOH</td>
<td>760(10)</td>
<td>40</td>
</tr>
<tr>
<td>$^{39}K$</td>
<td>KH$_2$PO$_4$</td>
<td>797(2)</td>
<td>10</td>
</tr>
<tr>
<td>$^{11}B$</td>
<td>H$_3$BO$_3$</td>
<td>1285(5)</td>
<td>30</td>
</tr>
<tr>
<td>$^{10}B$</td>
<td>HBO$_2$</td>
<td>1330(5)</td>
<td>50</td>
</tr>
</tbody>
</table>

The quadrupole Hamiltonian of a spin $5/2$ nucleus is:

$$\hat{H}_Q = \frac{e^2 q Q}{40} \left( 3 I_z^2 - 35/4 + \frac{1}{2} \eta (I_+^2 + I_-^2) \right)$$
XIV.4

If magnetic base states aligned along the principal axes of the electric field gradient are used, the Hamiltonian can easily be split into two $3 \times 3$ matrices:

\[
\begin{pmatrix}
\frac{e^2qQ}{40} & \sqrt{10} \eta & 0 \\
\sqrt{10} \eta & -8 & \sqrt{18} \eta \\
0 & \sqrt{18} \eta & -2
\end{pmatrix}
\]

Then the system is composed of three doubly degenerate energy levels with energies derived from the solution of the cubic secular equation.

\[
\lambda^3 - 28(3 + \eta^2) \lambda - 160(1 - \eta^2) = 0 \quad \text{(XIV.1)}
\]

There are three real roots which can be found numerically as a function of $\eta$. Since a spin $\frac{3}{2}$ nucleus has three energy levels there are three different transitions (all of which turn out to be allowed) and from any two of the three transition frequencies $e^2qQ$ and $\eta$ can be calculated.

If the roots of equation XIV.1 are $L_1$, $L_2$, and $L_3$, where $L_1 > L_2 > L_3$, then the three energy levels are $\frac{e^2qQ}{40}L_1$, $\frac{e^2qQ}{40}L_2$, and $\frac{e^2qQ}{40}L_3$, and the energy differences, $\frac{e^2qQ}{40}(L_1 - L_3)$, $\frac{e^2qQ}{40}(L_1 - L_2)$, and $\frac{e^2qQ}{40}(L_2 - L_3)$ correspond to the three measured transition frequencies. Then the ratio of any two transition frequencies is a function of $\eta$ alone. This property was used to calculate $e^2qQ$ and $\eta$ from the experimental data. Using a computer, the ratio of two of the calculated transition frequencies was compared with the ratio of the corresponding two measured quadrupole frequencies while $\eta$ was varied from 0 to 1. At one value of $\eta$ the two ratios were equal and this value of $\eta$ was taken to be the
assymetry parameter of the field gradient at the spin $\frac{5}{2}$ site. Once $\gamma$ has been obtained it is a simple operation to calculate $e^2\nu Q$ using any one of the quadrupole frequencies.

Three spin $\frac{5}{2}$ nuclei have been run - $^{27}\text{Al}$, $^{17}\text{O}$ and $^{25}\text{Mg}$. The measured frequencies, linewidths and calculated $e^2\nu Q$'s and $\gamma$'s are listed in table XIV.2. In aluminum hydroxide two inequivalent sites were found. They were distinguished with the aid of double irradiation techniques. The $H_2^0$ ice Ih was run two years ago by D.T. Edmonds and A. Zussman (73). In the ice II sample the peaks of the three lines do not satisfy $\nu = \nu_1 + \nu_3$ precisely so the error limits in the frequencies have been increased. The magnesium chloride hydrate spectrum is not clearly understood. There appear to be two inequivalent sites but in each case $\nu_1$ is quite different from $\nu_1 + \nu_3$.

### TABLE XIV.

<table>
<thead>
<tr>
<th>nucleus</th>
<th>compound</th>
<th>transition frequency</th>
<th>line-width</th>
<th>$e^2\nu Q$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{27}\text{Al}$</td>
<td>Al(OH)$_3$</td>
<td>site I</td>
<td>2170(10)</td>
<td>80</td>
<td>4670(20)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1360(10)</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>810(10)</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>site II</td>
<td>990(15)</td>
<td>100</td>
<td>1970(20)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>540(10)</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>450(10)</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>$^{17}\text{O}$</td>
<td>Ice Ih</td>
<td>(73)</td>
<td>3390(20)</td>
<td>100</td>
<td>6532(20)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1747(5)</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1650</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{17}\text{O}$</td>
<td>Ice II</td>
<td></td>
<td>3590(20)</td>
<td>120</td>
<td>7030(40)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1910(10)</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1705(10)</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>$^{25}\text{Mg}$</td>
<td>$\text{MgCl}_2\cdot 4\text{H}_2\text{O}$</td>
<td></td>
<td>1715.5</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1560(10)</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1350(10)</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>445(5)</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>195(5)</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

Of the quadrupolar nuclei which have been observed with
our technique the one whose spectra have been the most complicated to analyse is boron. A naturally occurring boron sample contains 81% boron 11 of spin 3/2 and 19% boron 10 of spin 3 so a spectrum should yield not only $e^2qQ$ and $\eta$ but also a value for the ratio $(e^2qQn_\alpha)/(e^2qQn_\beta)$.

The quadrupole spectrum of a spin 3/2 nucleus, as described earlier, consists simply of a single line at the frequency $e^2qQ/(1 + \eta/3)^{1/2}$ but a spin 3 nucleus has a more complicated spectrum. If the quadrupole Hamiltonian is written in the form:

$$
\mathcal{H}_Q = \frac{e^2qQ}{2I(2I-1)} (V_{xx}I_x^2 + V_{yy}I_y^2 + V_{zz}I_z^2)
$$

it is equivalent to the Hamiltonian describing the rotation of an asymmetric - top molecule (16 page 17)

$$
\mathcal{H}_o = \frac{1}{2M_x}J_x^2 + \frac{1}{2M_y}J_y^2 + \frac{1}{2M_z}J_z^2
$$

where the $M$'s represent moments of inertia and the $J$'s the components of angular momentum. Asymmetric top rotational spectra have been studied in detail in microwave spectroscopy and the solutions of the Hamiltonian have been tabulated (74) for several nuclear spins including spin 3. Making use of this equivalence the seven eigenvalues of a spin 3 nucleus in an electric field gradient are found to be:

$$
E = -\frac{e^2qQ}{5} + \frac{e^2qQ}{20} W
$$

where the $W$'s are given by the solutions of these equations:

$$
W - 4 = 0
$$

$$
W^2 - 4W - 60 = 0
$$

$$
W^2 - (10 - 6\eta) W + 9 - 5\eta - 15\eta^2 = 0
$$

The energy levels of a spin 3 nucleus are plotted as a
function of η in figure XIV.1.

Quadrupole spectra were obtained from two boron glasses B\textsubscript{2}O\textsubscript{3}.3H\textsubscript{2}O and B\textsubscript{2}O\textsubscript{3}.H\textsubscript{2}O. The transition frequencies and linewidths are listed in table XIV.3. Because \textsuperscript{11}B is four times as abundant as \textsuperscript{10}B and its gyromagnetic ratio is three times as large, the one very intense line in both spectra with more area underneath than any of the other lines was attributed to \textsuperscript{11}B. This choice was supported by the experimental evidence from an NMR study of \textsuperscript{11}B in the same two boron glasses(75).

**Table XIV.3**

Quadrupole data on boron

<table>
<thead>
<tr>
<th>nucleus</th>
<th>frequency (kHz)</th>
<th>linewidth (kHz)</th>
<th>\textsuperscript{10}B transition in figure XIV.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textsuperscript{10}B</td>
<td>2410(15)</td>
<td>30</td>
<td>A to F</td>
</tr>
<tr>
<td>\textsuperscript{10}B</td>
<td>1335.5(1)</td>
<td>3</td>
<td>D or E to F</td>
</tr>
<tr>
<td>\textsuperscript{11}B</td>
<td>1285(5)</td>
<td>30</td>
<td>C to D or E</td>
</tr>
<tr>
<td>\textsuperscript{10}B</td>
<td>760(15)</td>
<td>50</td>
<td>A to C</td>
</tr>
<tr>
<td>\textsuperscript{10}B</td>
<td>315(10)</td>
<td>60</td>
<td></td>
</tr>
</tbody>
</table>

\[ e^2 q B = 5340(4) \text{ or } 5355(4) \]
\[ η = 0.0029(4) \]

<table>
<thead>
<tr>
<th>nucleus</th>
<th>frequency (kHz)</th>
<th>linewidth (kHz)</th>
<th>\textsuperscript{10}B transition in figure XIV.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textsuperscript{10}B</td>
<td>2493(5)</td>
<td>20</td>
<td>A to F</td>
</tr>
<tr>
<td>\textsuperscript{10}B</td>
<td>1377(5)</td>
<td>20</td>
<td>D to F</td>
</tr>
<tr>
<td>\textsuperscript{11}B</td>
<td>1330(5)</td>
<td>50</td>
<td>A to D</td>
</tr>
<tr>
<td>\textsuperscript{10}B</td>
<td>1118.5(1)</td>
<td>8</td>
<td>B to D and E</td>
</tr>
<tr>
<td>\textsuperscript{10}B</td>
<td>950(10)*</td>
<td>40</td>
<td>B to C</td>
</tr>
<tr>
<td>\textsuperscript{10}B</td>
<td>405(5)</td>
<td>40</td>
<td>A to C</td>
</tr>
<tr>
<td>\textsuperscript{10}B</td>
<td>173(5)</td>
<td>30</td>
<td>A to C</td>
</tr>
</tbody>
</table>

*This may be two lines close together
Figure XIV.1. The energy levels of a spin 3 nucleus as a function of $\eta$. 

Energy in units of $\hbar^2/2\omega$.
As in the spin \(\frac{5}{2}\) case the ratio of any two transition frequencies for \(^{10}\text{B}\) is a function of \(\eta\) alone, so if ratios of transition frequencies are compared with ratios of the energy differences in figure XIV.1 for the whole range of \(\eta\), at the experimental value of \(\eta\) the two sets of ratios should be identical. This process was carried out by computer and for both of the glasses there were two regions of \(\eta\) where both sets of ratios were roughly equal - between 0 and 0.1 and between about 0.8 and 1. Closer examination revealed that the region between 0 and 0.1 was the more likely region. This is supported, in \(\text{B}_2\text{O}_3\cdot3\text{H}_2\text{O}\) at least, by the fact that boron is in a nearly axially symmetric environment (76).

From the energy level diagram for \(\eta = 0\) to \(\eta = 0.1\) in figure XIV.2, it can be seen that some energy differences such as D or E to F or A and A to F are almost independent of \(\eta\) while the B to C energy difference is very dependent on \(\eta\). The first type of transitions will be useful in determining \(\epsilon^2\eta Q\) and the latter for determining \(\eta\). The assignments of the boron 10 lines are listed in table XIV.3. For \(\text{B}_2\text{O}_3\cdot3\text{H}_2\text{O}\) \(\epsilon^2\eta Q\) was calculated from the narrow line at 1335.5 KHz which corresponds to a transition from D or E to F. If the transition is from D to F \(\epsilon^2\eta Q^{10\text{B}}\) is 1335.5(1)/4.9822 \(X\) 20 = 5340 (4) KHz and if it is from E to F \(\epsilon^2\eta Q^{10\text{B}}\) is 1335.5(1)/5.0017 \(X\) 20 = 5355(4) KHz. With either assignment \(\eta\) is found to be 0.029(4) using the line at 315 KHz and the other lines at 2410 and 760 KHz are accounted for within the experimental error.

In \(\text{B}_2\text{O}_3\cdot3\text{H}_2\text{O}\) \(\epsilon^2\eta Q\) was found using the transition at
Figure XIV.2. The energy levels of a spin 3 nucleus in the region between $\eta = 0$ and $\eta = 0.1$. In the text the levels are referred to by the letters A, B, C... on the right.
1118.5 KHz to be 11 18.5(1) A.0722 X 20 = 5493(5) KHz and η was calculated to be 0.069(3) from the transitions at 405 and 173 KHz.

Now that η is known it is possible to calculate accurate values for e^2 q^\nu B. For B_2 O_3 \cdot 3H_2 O e^2 q^\nu B = 2 \times 1265(5) = 2570(10) \text{ and for } B_2 O_3 \cdot H_2 O e^2 q^\nu B = 2660(10). \text{ Using the data from } B_2 O \cdot 3H_2 O \text{ the ratio } (e^2 q^\nu B)/(e^2 q^\nu B) \text{ is found to be } 2.078(10) \text{ or } 2.084(10) \text{ depending on the assignment of the transition at } 1335.5 \text{ KHz. For } B_2 O_3 \cdot H_2 O \text{ it is found to be } 2.065(10). \text{ The fact these are not equal is not as serious as one might expect because, although the actual field gradients are identical since the nuclear sites are the same, the motional averaging processes which effect the measured quadrupole constants may be different for the two isotopes due to their different masses. This difference in motional averaging will not necessarily be the same in different molecules (10 page 48).}

This has not been the first NQR investigation on boron 10. In 1952, H. Dehmelt (77) measured the quadrupole spectra of ^10 B and ^11 B in two forms of B(CH_3)_3 and B(C_2 H_5)_3. He found the ratio (e^2 q^\nu ^{10} B)/(e^2 q^\nu ^{11} B) to be 2.084(2) for all three samples. It is interesting that the linewidths he measured for ^10 B were of order 2 to 5 KHz in sharp contrast to the broad lines ~30 KHz found in this study.

In conclusion it would appear that the laboratory frame double resonance method is ideally suited for NQR investigations in a large number of nuclei. The most serious limitation in this project was, as always, the difficulty in finding a sample with appropriate T_1's.
Appendix I

The following is a complete list of the nitrogen quadrupole frequencies and quadrupole constants obtained in the research for this thesis. Most of this data has already appeared in the literature. The grouping of the quadrupole frequencies and the assignment to particular sites has been carried out as described in Chapter X. Unless noted otherwise the errors in the frequencies are 1 KHz or less.

For several of the amino acids the DL crystalline form gave the same quadrupole spectrum as the L form. In these cases the samples were suspected not to have a true DL structure but rather to be composed of an equal mixture of L and D crystals.
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<th>ν⁻</th>
<th>ν₀</th>
<th>$\eta$</th>
<th>Shifts in $\nu^2$Q on deuteration</th>
<th>Comments</th>
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<td>( \nu^- )</td>
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<td>$\gamma^-$</td>
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<td>$\gamma^-$</td>
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<td>684</td>
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<td>1923(5)</td>
<td>570(10)</td>
<td>2941(6)</td>
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<td>( \nu^- )</td>
<td>( \nu_0 )</td>
<td>( e^2Q )</td>
<td>( \eta )</td>
<td>Shifts in ( e^2Q ) deuteration</td>
<td>Comments</td>
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Appendix II

The following is a list of the deuterium data collected during the research for this thesis. Some complicated spectra containing overlapping lines from many sites were impossible to account for and have not been included. A considerable amount of the data on amino acids has been published in reference (79) and the data on acetamide has been published in reference (62). For the ND$_2$ and OD$_2$ sites containing fine structure, the $e^2qQ$'s and $\eta'$'s have been calculated using the method of Chapter VIII. The mean $e^2qQ$'s and $\eta'$'s for these sites are given in Table VIII 3. Unless noted otherwise the errors in the frequencies are 0.1 KHz or less. For those compounds which have been used for Figures XII 1,2,3 the relevant data has been assigned identification numbers and letters and the structure reference is given.
<table>
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<th>Chemical Formula</th>
<th>Site</th>
<th>Identification number</th>
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<th>$\gamma^+$</th>
<th>$\gamma^-$</th>
<th>$e^2qQ$</th>
<th>$\eta$</th>
<th>Struct. ref.</th>
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<td></td>
<td>$\gamma^+$ at 123.2 + unresolved lines between 115.5 and 120.2</td>
<td>$\gamma^-$ lines at 160.7, 152.3</td>
<td>mean $e^2qQ$ 216.9</td>
<td>mean $\eta$ 0.115</td>
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<td>COO$^-$D$_2$O</td>
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<td>$\gamma^-$ lines at 169.5, 168.5</td>
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Note: The table contains data for various compounds with their respective chemical formulas, sites, and measured properties such as $\gamma_+$, $\gamma_-$, $e^2qQ$, and $\eta$.
References

18. R.G. Barnes, Adv. in Nuclear Quadrupole Resonance 1, 335 (1974).

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68. T.F. Koetzle and M.S. Lehmann, a review on neutron diffraction studies to be published by North Holland in a book on hydrogen bonding edited by F. Schuster.