

**NMR Studies of Anisotropic Nuclear Spin Interactions in Solids:
The Importance of Examining NMR Interaction Tensors**

by

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Submitted in partial fulfilment of the requirements
for the degree of Doctor of Philosophy

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To My Father

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Abstract

A combination of solid-state nuclear magnetic resonance (NMR) spectroscopy and *ab initio* molecular orbital calculations has been employed in this thesis to investigate the fundamental origins of anisotropic nuclear spin interactions. Valuable information has been obtained by examining the orientation-dependent or anisotropic nature of these spin interactions rather than the orientational average measured in solution NMR spectroscopy. Unequivocal experimental evidence is provided for the first time in this thesis for an anisotropic indirect spin-spin coupling tensor, **J**. Analysis of data obtained from phosphorus-31 single-crystal NMR investigations involving two mercury-phosphine complexes has revealed large anisotropies in the ^{199}Hg - ^{31}P **J** tensors, on the order of 4-5 kHz. These findings provide conclusive evidence that indirect spin-spin coupling mechanisms other than Fermi contact make important contributions to the transmission of nuclear spin information between ^{199}Hg and ^{31}P nuclei, contrary to previous assumptions in the literature. Valuable information concerning the orientation of the phosphorus chemical shift tensors in these complexes has also been obtained, representing only the second single-crystal study of the phosphorus chemical shift tensor for a metal-phosphine complex. The work in this thesis provides the first measurements of the orientation of the carbon chemical shift tensor for the thiocarbonyl group, C=S. Both experimental and theoretical evidence indicate that the orientations of the carbon chemical shift tensors for the C=S and C=O fragments are qualitatively analogous, contrary to the conclusions of an earlier investigation. A comparison of experimental and theoretical carbon chemical shift tensor data within a series of related carbonyl and thiocarbonyl-containing molecules reveals that the well-known carbon deshielding observed for the C=S fragment is not due to variations in $n \rightarrow \pi^*$ transition energies, dispelling earlier misconceptions in the literature.

List of Symbols and Abbreviations

Symbols

$\S$	-	section
$\mathcal{H}$	-	Hamiltonian operator
I	-	nuclear spin angular momentum operator
I_z	-	z-component spin angular momentum operator
I	-	nuclear spin angular momentum quantum number
I_+, I_-	-	raising and lowering operators
$\mu, \hat{\mu}$	-	magnetic dipole moment and operator
m_z	-	z-component nuclear spin angular momentum
$h=2\pi\hbar$	-	Planck's constant
γ	-	magnetogyric ratio
B_0	-	external magnetic field strength
$\mathbf{B}_0$	-	external magnetic field vector
$ \alpha\rangle, \beta\rangle$	-	nuclear spin states
B_{eff}	-	effective magnetic field
ν_0, ν	-	Larmor frequency and resonance frequency
σ	-	chemical shielding tensor
$\sigma_{11}, \sigma_{22}, \sigma_{33}$	-	principal components of chemical shielding tensor
σ_{iso}	-	isotropic chemical shielding
$\delta_{11}, \delta_{22}, \delta_{33}$	-	principal components of chemical shift tensor
δ_{iso}	-	isotropic chemical shift

Ω	-	span of chemical shift tensor
$\mathbf{r}, r$	-	dipolar vector and its magnitude
μ_0	-	permeability of free space
R_{DD}	-	direct dipolar coupling constant
$\mathbf{D}$	-	dipolar tensor
(θ, ϕ)	-	polar angles defining $\mathbf{r}$ in lab frame
$\mathbf{J}$	-	indirect spin-spin coupling tensor
$\mathbf{J}'$	-	symmetric part of $\mathbf{J}$ tensor
J_{zz}, J_{yy}, J_{xx}	-	principal components of $\mathbf{J}$ tensor
$\Delta J = J_{\parallel} - J_{\perp}$	-	anisotropy in $\mathbf{J}$
J_{iso}	-	isotropic indirect spin-spin coupling constant
$R_{eff} = R_{DD} - \Delta J/3$	-	effective dipolar coupling constant
λ	-	general second-rank tensor
$\cos \Phi$	-	direction cosine
ψ	-	rotation angle in single-crystal experiment
(α, β, γ)	-	Euler angles
e, m	-	electronic charge and mass
L	-	orbital angular momentum operator
$ 0\rangle, k\rangle$	-	ground and excited electronic state wave function
E_0, E_k	-	energy of ground and excited electronic state, k
σ^d	-	diamagnetic contribution to chemical shielding
σ^p	-	paramagnetic contribution to chemical shielding

μ_B	-	Bohr magneton
$\delta(r)$	-	Dirac delta function
${}^3\Delta E$	-	average triplet excitation energy
$ S_N(0) $	-	<i>s</i> -electron density at nucleus <i>N</i>
$P_{s_N s_{N'}}$	-	bond order between nuclei <i>N</i> and <i>N'</i>
α_N	-	<i>s</i> -character of hybrid orbital at nucleus <i>N</i>
ξ	-	phase angle in single-crystal experiment
$\Delta\nu_{11}, \Delta\nu_{22}, \Delta\nu_{33}$	-	dipolar splittings at $\delta_{11}, \delta_{22}, \delta_{33}$
S	-	electron spin operator

Abbreviations

AO	-	atomic orbital
CHF	-	coupled Hartree-Fock
CP	-	cross-polarization
CS	-	chemical shift
Cy	-	cyclohexyl
FC	-	Fermi contact mechanism
GIAO	-	gauge-including atomic orbitals
HOMO	-	highest occupied molecular orbital
IGLO	-	individual gauge for localized molecular orbitals
LORG	-	localized orbital - local origin
LR	-	Lawesson's reagent

LUMO	-	lowest unoccupied molecular orbital
MAS	-	magic-angle-spinning
MO	-	molecular orbital
NMR	-	nuclear magnetic resonance
OD	-	orbital diamagnetic mechanism
OP	-	orbital paramagnetic mechanism
PAS	-	principal axis system
Ph	-	phenyl
SCF	-	self-consistent-field
SD	-	spin-dipolar mechanism
TEPS	-	tetraethyldiphosphine disulfide
VAS	-	variable-angle-spinning

All other symbols and abbreviations correspond to their standard usage.

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Chapter 1

Introduction

In 1995, the spectroscopic technique known as nuclear magnetic resonance (NMR) celebrated its 50th birthday. Since the initial joint discoveries of NMR in bulk matter by Purcell, Torrey, and Pound (1) as well as Bloch, Hansen, and Packard (2), the field has undergone a very rapid and diverse expansion. Today, NMR spectrometers can be found in a wide variety of academic and industrial settings. As well, many scientific journals and reviews now exist which are dedicated exclusively to advances and/or applications of NMR spectroscopy. The fundamental origins of this explosive growth can be related to the unique manner in which this spectroscopy probes molecular and electronic structure. In contrast with many of the other spectroscopies which measure electronic energy levels, NMR monitors quantized nuclear energy levels. As will become apparent in Chapter 2, it is the sensitivity of these levels to the motion of other nuclei and electrons which is the foundation of the sensitive link between NMR spectroscopy and structure. Furthermore, in contrast with diffraction techniques where long-range molecular order is so vitally important, these energy levels are only sensitive to the *local* nuclear environment. Consequently, nuclei observed in an NMR experiment act as strategic probes of short-range molecular structure, making the technique amenable to amorphous and other non-crystalline materials where diffraction techniques are of limited utility. Finally, NMR spectroscopy is also unique in that the excited nuclei have relatively long lifetimes and "relax" through an exchange of energy with the

environment, commonly termed the lattice. This exchange is highly motion-sensitive so that NMR relaxation studies are capable of providing valuable information concerning intramolecular rotations and disorder.

The structural sensitivity of nuclear magnetic moments was recognized very early in the history of NMR. In 1948, George Pake was able to measure the internuclear proton separation in $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ by observing the direct dipolar interaction between proton nuclei in the ^1H NMR spectrum of a solid powder sample (3). Shortly thereafter, it was recognized that the precise magnetic moment of a given nucleus measured from solution NMR spectra was sensitive to the compound used, marking the discovery of the chemical shift (δ) effect (4, 5, 6). Around the same time, multiplet patterns were observed in NMR spectra of liquids due to a coupling interaction with other nuclear magnetic moments in the sample and transmitted *via* the bonding electrons connecting the coupled nuclei (7, 8, 9). The magnitude of the multiplet splittings and the multiplicity were found to be sensitive to the nature of the nuclei coupled as well as the local nuclear environments. This phenomenon is known as indirect spin-spin (J) coupling. Given the diagnostic value of each of these parameters, it is not surprising that such discoveries quickly led to a "transfer of control" of NMR spectroscopy from the domain of the physicist to that of the chemist. Also recognized very early was the fact that, in general, these NMR diagnostic parameters should vary with the orientation of a molecule in the external magnetic field. Indeed, Pake had demonstrated this for the case of the dipolar interaction in his studies of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Unfortunately, NMR spectra of solid samples were often found to give broad, featureless lines due to strong dipolar couplings, masking

the orientation dependence theoretically predicted by Ramsey for the weaker chemical shift (10) and J (11) interactions. Thus, the early NMR literature quickly became dominated by studies of solutions where rapid molecular tumbling eliminates dipolar interactions. Unfortunately, also eliminated in solution is the orientation dependence of chemical shifts and J couplings; only an average value is observed.

Many of the traditional ideas chemists have concerning the structural dependencies of chemical shifts and J couplings emerged during this early solution-dominated period. For the case of chemical shifts, it became fashionable to correlate and thus "interpret" average chemical shifts in terms of numerous structural features such as charge densities, electronic excitation energies, bond orders, *etc.*; experiments still widely performed today. Similar approaches were employed for applications of J couplings, the most popular being correlations with the s character of the bond(s) joining the coupled nuclei. Although experiments of this nature are potentially informative, a fundamental assertion of this thesis is that concrete experimental evidence as to the origins of trends observed in chemical shifts or J couplings cannot be obtained by examining just the average or isotropic value. Such evidence can only be obtained by investigating the orientation dependence of these interactions. Herein lies the focus of this thesis.

During this early stage in the history of NMR, several key experiments were being devised in order to increase the resolution and sensitivity achieved from NMR spectra of solid samples. Most notable for the purposes of this thesis is the innovative work of Pines, Gibby, and Waugh in the early 1970s (12), who showed how a combination of techniques known as cross-polarization (CP) and high-power proton

decoupling lead to both sensitivity and resolution gains. The sensitivity increase is due to the CP component of this experiment, a technique designed to increase the equilibrium magnetization for a magnetically dilute nucleus such as ^{13}C , ^{15}N , or ^{29}Si by transferring magnetization from an abundant source, most commonly the proton nucleus. The manner in which this transfer was accomplished was based upon an earlier double-resonance experiment devised by Hartmann and Hahn (13). The advent of the CP experiment also meant that the spectroscopist could now apply excitation pulses in intervals defined by the relaxation time of the abundant spins, normally much shorter than that of the dilute spins, thereby decreasing the overall time required to acquire a spectrum. The resolution gain achieved in this experiment is due to the application of high-power proton decoupling during spectral acquisition which removes line broadening arising from strong dipolar interactions with protons. Thus, this ingenious experiment suddenly made it feasible to examine the previously inaccessible orientation-dependent nature of chemical shifts and weaker spin-spin couplings involving these magnetically dilute nuclei. Consequently, given the greater information content available from the three-dimensional nature of the NMR parameters, this pioneering work fuelled an intense interest in the application of solid-state NMR to structural studies, an area which continues to expand at extraordinary levels today.

The primary objective of this thesis is to clearly illustrate the advantages of examining the orientation dependence of NMR interactions such as chemical shifts and J couplings rather than the orientational average observed in solution NMR studies. It will be demonstrated how such an approach affords a much more detailed insight into the

structural origins of these parameters. In order to achieve this objective, solid-state NMR spectroscopy has been employed to address two questions of fundamental importance. The first of these involves whether the ^{199}Hg - ^{31}P J coupling is orientation dependent or not, a very important inquiry given that an orientation-dependent J coupling is mediated by mechanisms other than Fermi contact. Traditionally, ^{199}Hg - ^{31}P J couplings have been interpreted exclusively in terms of the Fermi contact mechanism. The second question addressed in this thesis is "what are the dominant factors dictating the large variations observed in the isotropic carbon chemical shifts for the carbonyl and thiocarbonyl groups?" Traditionally, these variations have been interpreted as due to differences in $n \rightarrow \pi^*$ transition energies based on the results of correlations involving isotropic carbon chemical shifts. The results of this work are very exciting and have far-reaching implications concerning how chemists understand the origins of both of these interactions.

The remainder of this thesis is organized in the following manner. In Chapter 2, the necessary background information will be provided. This will involve a discussion of each of the relevant NMR interaction Hamiltonians as well as the experiments employed in this thesis for characterizing these interactions. Also included is a discussion of the structural origins of chemical shifts and J couplings, developed according to the theories of Ramsey. In Chapter 3, the question concerning the nature of ^{199}Hg - ^{31}P J couplings will be addressed by investigating two mercury-phosphine complexes using single-crystal NMR studies. The results of this work represent the most reliable evidence thus far for the existence of an orientation-dependent J coupling. As

well, valuable information concerning the phosphorus chemical shift tensors in these complexes is provided. A solid-state NMR investigation into the carbon chemical shifts within the carbonyl and thiocarbonyl groups is the subject of Chapter 4. Also of primary concern here will be the ability of *ab initio* chemical shielding calculations to provide valuable insight into the experimental findings. Finally, in Chapter 5 a summary is provided along with some possible extensions of this work.

Chapter 2

Background Theory

The purpose of the present chapter is to provide the necessary background information essential for an understanding of the science contained in this thesis. The first section of this chapter, §2.1, provides a description of the relevant NMR interaction Hamiltonians, with particular emphasis on how these are manifested in the NMR spectra of solids. In §2.2, the experimental solid-state NMR techniques employed for measuring these NMR parameters are described. Finally, §2.3 is devoted to a theoretical description of the physical origins of the NMR interactions and the manner in which these are related to molecular and electronic structure, material upon which much of the discussion and conclusions of this work are founded.

2.1 Anisotropic Nuclear Spin Interactions

The basis of the NMR experiment as well as its paramount importance to the study of molecular and electronic structure lies in the interaction between magnetic fields and the microscopic charged particles that constitute all atomic and molecular systems. In general, the NMR Hamiltonian for a diamagnetic solid can be written as:

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_{CS} + \mathcal{H}_{DD} + \mathcal{H}_J + \mathcal{H}_Q + \mathcal{H}_{RF} \quad (2.1)$$

where $\mathcal{H}_Z$ is the Zeeman interaction, $\mathcal{H}_{CS}$ is the chemical shielding interaction, $\mathcal{H}_{DD}$ is the direct dipole-dipole interaction, $\mathcal{H}_J$ is the indirect spin-spin coupling interaction, and $\mathcal{H}_Q$

is the quadrupolar interaction. The fundamental interaction that is the basis of nuclear magnetic resonance spectroscopy is the Zeeman interaction. The remaining terms describe perturbations to the Zeeman energy levels and are the origin of the unique sensitivity of NMR spectroscopy to molecular and electronic structure. The final term in the Hamiltonian, $\mathcal{H}_{RF}$, describes the interaction between the nuclear magnetic moments and the magnetic field component of the radiofrequency radiation which is applied to excite a nuclear spin system. Following a discussion of the Zeeman interaction, the remainder of §2.1 will be devoted to describing each of the interactions essential to the research presented in later chapters of this thesis; namely $\mathcal{H}_{CS}$, $\mathcal{H}_{DD}$, and $\mathcal{H}_J$. For a more in-depth treatment, the interested reader is referred to monographs by Abragam (14), Ernst, Bodenhausen, and Wokaun (15), Gerstein and Dybowski (16), Haeberlen (17), Mehring (18), Slichter (19), Schmidt-Rohr and Spiess (20), Spiess (21), Stejskal and Memory (22) as well as the review articles by Smith *et al.* (23).

2.1.1 The Zeeman Interaction

Depending upon nuclear composition, a nucleus can possess an intrinsic property known as nuclear spin angular momentum. The magnitude of the nuclear spin angular momentum is given by:

$$I = \hbar[I(I + 1)]^{1/2} \quad (2.2)$$

where I is the nuclear spin quantum number and is either integral or half-integral and $\hbar$ is $h/2\pi$ where h is Planck's constant. For those nuclei with $I=0$, NMR spectroscopy is

not possible. However, for nuclei that possess a non-zero spin angular momentum, there exists an associated magnetic dipole moment which is given by:

$$\mu = \gamma I = \gamma \hbar [I(I + 1)]^{1/2} \quad (2.3)$$

where γ is the nuclear magnetogyric ratio, a constant for nuclei of a particular isotope.

Given that angular momentum is a vector property, nuclear spin angular momentum is characterized by both a magnitude and direction. The direction is specified by another quantum number, m_I , which may take on $2I+1$ values ranging from $-I$ to $+I$ in unit increments. In the absence of an external magnetic field, the energy of a nucleus is independent of direction. However, upon application of an external magnetic field, the nuclear energy is quantized according to the orientation of the nuclear magnetic dipole moment in the applied field. This phenomena, known as the Zeeman interaction, results in a lifting of the degeneracy of the $2I+1$ orientations corresponding to the allowed values of the m_I quantum number. It is customary to take the external magnetic field direction as the z axis of the laboratory frame. Using this convention, the Zeeman Hamiltonian can be expressed as:

$$\hbar^{-1} \mathcal{H}_Z = -\mu \cdot B_o = -\gamma I \cdot B_o = -\frac{\gamma}{2\pi} B_o m_z \quad (2.4)$$

where m_z is the z -component of the nuclear spin angular momentum. The $2I+1$ energy levels that result are known as nuclear spin states. For example, for the case of an $I=1/2$ nucleus, there exists two spin states, $m_z = \pm 1/2$. The $m_z = +1/2$ level is usually denoted as the $|\alpha\rangle$ spin state and the $m_z = -1/2$ level as the $|\beta\rangle$ spin state. Transitions may be

induced between these states upon application of electromagnetic radiation of appropriate frequency. The selection rule governing this form of spectroscopy, known as nuclear magnetic resonance spectroscopy, is $\Delta m_z = \pm 1$. Thus, the radiation frequency required for transitions between the Zeeman spin states must satisfy the condition:

$$\nu_o = \frac{\gamma}{2\pi} B_o \quad (2.5)$$

This frequency, which falls in the radiofrequency portion of the electromagnetic spectrum, is known as the Larmor frequency and depends upon the magnetogyric ratio of the nucleus under observation as well as the strength of the applied magnetic field. For example, at an external magnetic field strength of 4.7 T, the Larmor frequency for the ^1H nucleus is 200 MHz while for the ^{13}C nucleus this frequency is 50.3 MHz.

There are two further points worth mentioning at this stage concerning the Zeeman interaction. Firstly, as a consequence of the small energy differences involved, the Boltzmann distribution at thermal equilibrium leads to very small population differences at normal temperatures. For example, $n_\beta/n_\alpha = 0.999968$ for proton nuclei in a macroscopic sample at 300 K in an external field of 4.7 T. As a result, NMR is a relatively insensitive form of spectroscopy which, for naturally occurring "dilute" nuclei, explains the common practice of sensitivity enhancement through isotopic enrichment. Two further methods of enhancing the sensitivity of an NMR experiment for a given isotope are moving to higher applied magnetic fields or working at lower temperatures. Secondly, it is clear that the strength of the Zeeman interaction is constant for a particular isotope at a given external field strength. If this were the only interaction

important in the NMR experiment, all NMR spectra for a particular isotope would consist of a single peak located at the nuclear Larmor frequency, regardless of the chemical species being examined! Molecular and electronic structure information that is embedded in an NMR spectrum originates from the remaining subtle interactions present in the NMR Hamiltonian that perturb the nuclear Zeeman spin states.

2.1.2 The Chemical Shielding Interaction

In the presence of an external magnetic field, the electrons in a chemical sample generate internal magnetic fields due to induced electronic motion. These secondary magnetic fields alter the strength of the applied magnetic field experienced at the nuclear site under observation which, in turn, modifies the resonance frequency condition of a nuclear spin. This phenomenon is known as the chemical shielding interaction. The *effective* magnetic field, B_{eff} , experienced by a nucleus in the presence of both an external magnetic field, B_o , as well as chemical shielding is given by $(1 - \sigma)B_o$ where σ represents the magnitude of the chemical shielding. The resonance frequency, ν , for such a nucleus is thus given by:

$$\nu = \frac{\gamma}{2\pi} B_{eff} = \nu_o (1 - \sigma) \quad (2.6)$$

In the absence of a spherical distribution of electronic charge, the shielding interaction will depend upon the orientation of a molecule with respect to the external magnetic field; it is anisotropic. The three-dimensional nature of the shielding interaction is described by a second rank Cartesian tensor (24), σ .

The Hamiltonian governing the chemical shielding interaction is as follows:

$$h^{-1} \mathcal{H}_{CS} = \boldsymbol{\mu} \cdot \boldsymbol{\sigma} \cdot \mathbf{B}_o \quad (2.7)$$

However, with the external magnetic field taken to be along the z direction and noting that the magnitude of the chemical shielding interaction is typically six orders of magnitude smaller than the Zeeman interaction, this Hamiltonian can be rewritten as:

$$h^{-1} \mathcal{H}_{CS} = \mu_z \sigma_{zz} B_o = \gamma I_z \sigma_{zz} B_o \quad (2.8)$$

Note that this Hamiltonian has the same form as that of the Zeeman Hamiltonian (*cf.* eq. 2.4). Thus, chemical shielding can be thought of as a tiny Zeeman interaction with the nuclear magnetic dipole moment interacting with an induced field of magnitude $\sigma_{zz} B_o$. Also, it is clear that these induced fields are a function of the external magnetic field strength; chemical shielding is a field-dependent phenomenon.

In general, the chemical shielding tensor is a 3×3 matrix defined by nine independent elements. A tensor of this form can be separated into symmetric and antisymmetric tensors (25) and, to first order, only the symmetric part of the chemical shielding tensor contributes to σ_{zz} . In the absence of symmetry, the symmetric part of $\boldsymbol{\sigma}$ is completely defined by six independent elements. These are normally specified with reference to an axis system in which the tensor is diagonal, known as the principal axis system (PAS). The three diagonal elements are known as the principal components of the chemical shielding tensor, denoted σ_{11} , σ_{22} , and σ_{33} . The convention maintained throughout this thesis is that σ_{33} is the most shielded component such that $\sigma_{33} \geq \sigma_{22} \geq$

σ_{11} . The remaining three variables required to define the symmetric part of σ are the Euler angles, which describe the rotations necessary to specify the orientation of the PAS relative to some reference frame. Note that this information can always be obtained from the eigenvalues and eigenvectors upon diagonalization of the chemical shielding tensor. For a nuclear environment in which the local site symmetry is greater than C_1 , the number of independent elements of the shielding tensor is reduced. A table specifying the number of independent elements of σ as a function of local point-group symmetry has been compiled by Buckingham and Malm (26).

From the preceding discussion it is clear that for nuclei in ordered molecular systems such as crystalline solids, the observed shielding, σ_{zz} , will, in general, be orientation dependent. This implies that the chemical shielding will depend upon the orientation of the magnetic field vector in the PAS of the chemical shielding tensor. Using directional cosines to specify this orientation according to the convention in Figure 2.1, the NMR resonance frequency for the case of a single-crystal sample can be written as:

$$\nu = \nu_o [1 - \sigma_{zz}] = \nu_o [1 - (\sigma_{11} \cos^2 \Phi_1 + \sigma_{22} \cos^2 \Phi_2 + \sigma_{33} \cos^2 \Phi_3)] \quad (2.9)$$

For the more common case of a powder sample, the individual crystallites can be thought of as tiny single crystals which are randomly oriented relative to the external magnetic field. This distribution of orientations generally leads to a distribution of resonance frequencies such that the resulting NMR spectrum exhibits a broad line shape commonly referred to as a powder pattern. An example of a powder pattern arising from

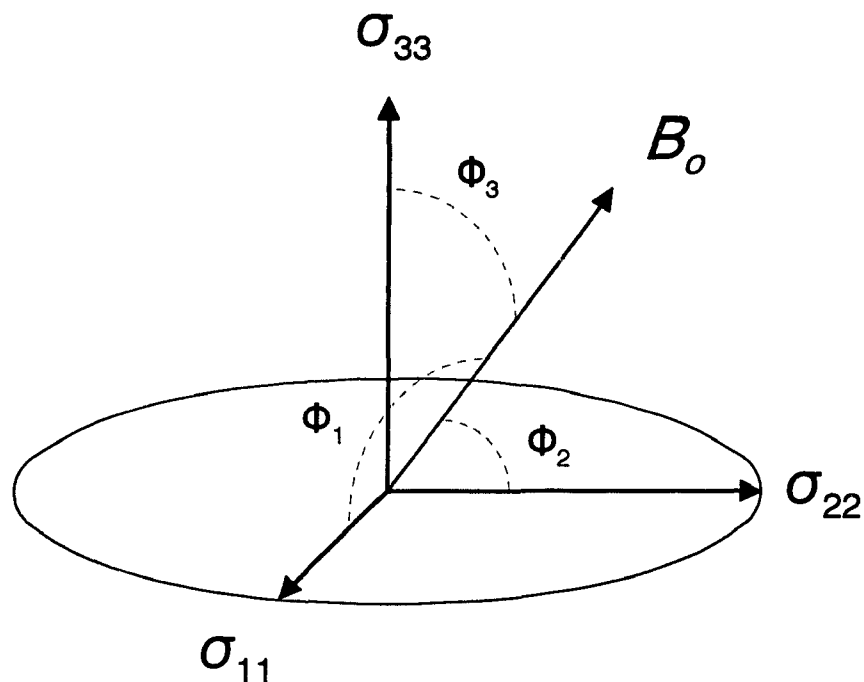


Figure 2.1 The orientation of the magnetic field vector relative to the principal axis system of the chemical shielding tensor is defined by the angles Φ_1 , Φ_2 , Φ_3 .

anisotropic chemical shielding is provided in Figure 2.2. The isotropic chemical shielding, $\sigma_{\text{iso}} = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33})$, represents an orientational average of the three-dimensional information available from the chemical shielding tensor. The span (27), $\Omega = \sigma_{33} - \sigma_{11}$, is a measure of the breadth of the powder pattern observed for an anisotropic chemical shielding tensor.

In closing this section, several concluding points are worth mentioning. Firstly, the total chemical shielding observed at a particular nuclear site can be thought of as

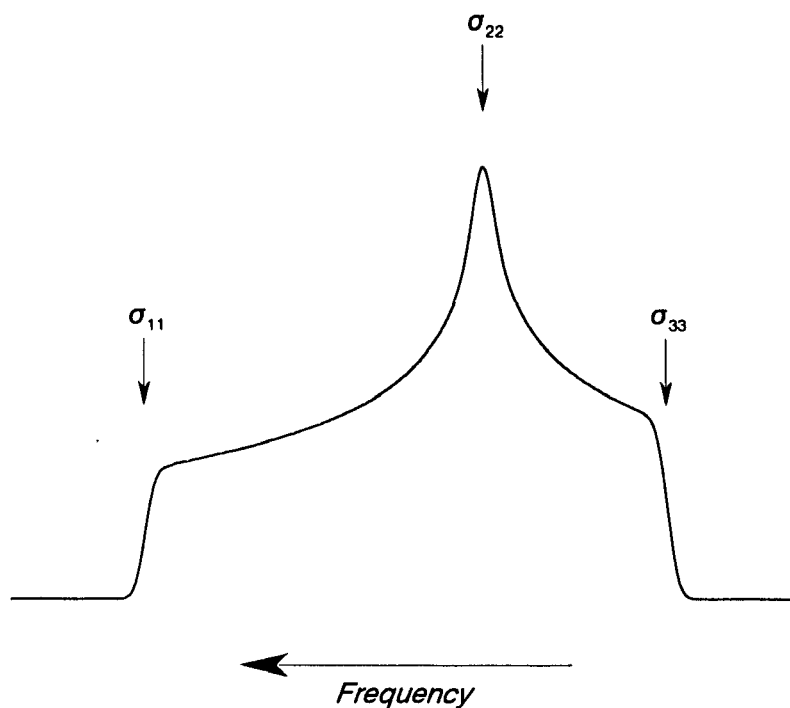


Figure 2.2 A typical powder pattern arising from anisotropic chemical shielding. The positions of the three principal components of the chemical shielding tensor, σ_{ii} , are also indicated.

arising from two distinct types of electronic motion in the presence of an external magnetic field. These are referred to as diamagnetic and paramagnetic shielding (10). Since a qualitative understanding of these two different modes of electronic motion is a prerequisite to Chapter 4 of this thesis, a detailed discussion of these is provided in §2.3.1. Secondly, the value of the chemical shielding is defined with respect to the bare nucleus. In practice, NMR spectra do not yield values for the shielding interaction, σ , but rather chemical shifts, δ , which quantify the difference in resonance frequencies between the nucleus of interest and the same nucleus in a suitably chosen reference

compound:

$$\delta(ppm) = \frac{\nu_{obs} - \nu_{ref}}{\nu_{ref}} \cdot 10^6 \quad (2.10)$$

In Figure 2.3, the difference between chemical shielding and shift scales is illustrated for the case of the ^{13}C nucleus. Given that δ is approximately equal to $\sigma_{ref} - \sigma_{obs}$, all that is available from routine NMR spectra are differences in nuclear magnetic shieldings. Only in cases where the value of the absolute shielding is known for at least one of the nuclei observed in an NMR spectrum can NMR be capable of yielding values for the

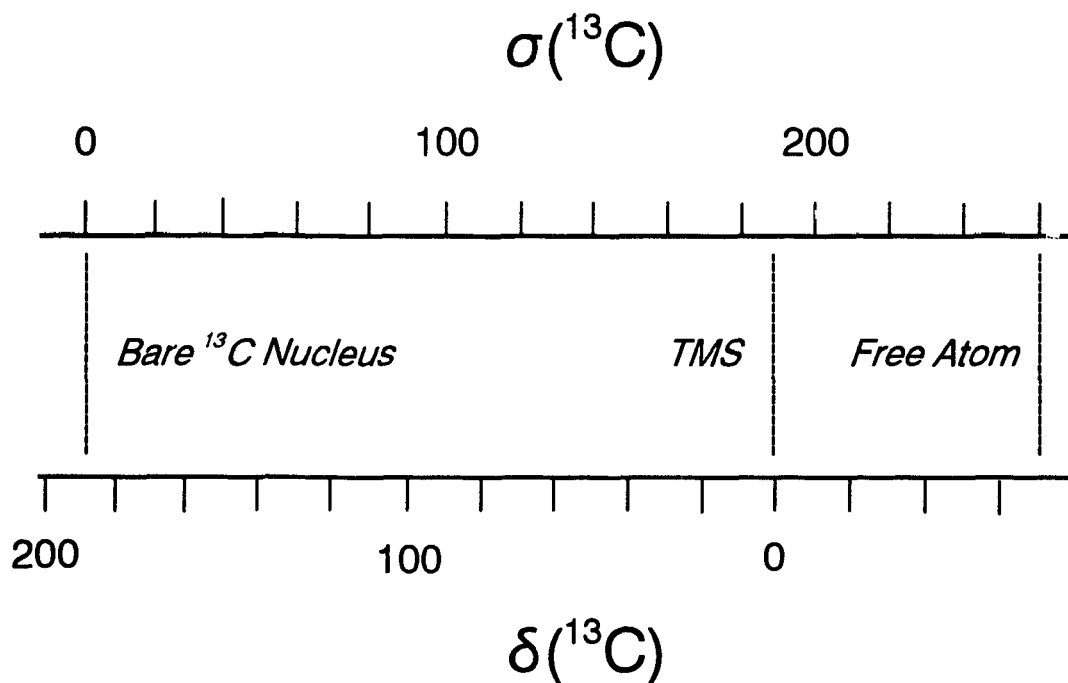


Figure 2.3 Diagram displaying the opposite behavior of the chemical shielding, σ , and chemical shift, δ , scales.

absolute shielding. For a discussion of various methods of establishing absolute shielding scales, the interested reader is referred elsewhere (28). The convention for the three principal components of the chemical shift tensor adopted in this thesis is $\delta_{11} \geq \delta_{22} \geq \delta_{33}$. Thus, δ_{33} and σ_{33} represent the most shielded components of the shift and shielding tensors, respectively.

2.1.3 The Direct Dipole-Dipole Interaction

We have seen that a nucleus with an intrinsic spin angular momentum has an associated magnetic moment with an energy that is quantized by the application of an external magnetic field. Furthermore, this energy is sensitive to internal magnetic fields in the vicinity of the nucleus that result from electronic motion in the atom or molecule. In a directly analogous manner, a second nuclear spin spatially located near this nucleus becomes another source of an internal magnetic field. These two spins can be thought of as tiny bar magnets which "feel" the effects of one another's magnetic fields. The effective magnetic field experienced by these nuclei will be different than the external magnetic field strength, thereby modifying the resonance frequency condition. This interaction is known as the direct dipolar interaction.

The Hamiltonian for the dipolar interaction can be derived from the classical expression for the interaction energy between two magnetic point dipoles, μ_I and μ_S , and is given by:

$$\mathcal{H}_{DD} = \gamma_I \gamma_S \hbar^2 \left[\frac{\mathbf{I}_I \cdot \mathbf{I}_S}{r^3} - 3 \frac{(\mathbf{I}_I \cdot \mathbf{r})(\mathbf{I}_S \cdot \mathbf{r})}{r^5} \right] \frac{\mu_o}{4\pi} \quad (2.11)$$

where $\mathbf{r}$ is the internuclear vector and r is the magnitude of this vector. Expanding the dot products in eq. 2.11, it can be shown that the dipolar Hamiltonian can be expressed as (29, 30):

$$\hbar^{-1}\mathcal{H}_{DD} = R_{DD}(\mathbf{I}_I \cdot \mathbf{D} \cdot \mathbf{I}_S) \quad (2.12)$$

where $\mathbf{D}$ is a symmetric tensor known as the dipolar tensor and R_{DD} is known as the direct dipolar coupling constant:

$$R_{DD} = \frac{\mu_o}{4\pi} \frac{\hbar}{2\pi} \frac{\gamma_I \gamma_S}{r_{IS}^3} \quad (2.13)$$

Choosing a reference frame such that the internuclear dipolar vector lies along the z axis, the dipolar tensor takes on the following form:

$$\mathbf{D} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix} \quad (2.14)$$

There are several important points to note concerning eq. 2.14. Firstly, the trace of the dipolar tensor or, equivalently, the sum of the diagonal elements is zero. Consequently, in solution NMR spectroscopy, peak positions are not influenced by the dipolar interaction. As well, given the fact that $\mathbf{D}$ is diagonal in eq. 2.14, the aforementioned reference frame represents the PAS of the dipolar tensor. Thus, the dipolar interaction is axially symmetric ($D_{xx} = D_{yy} \neq D_{zz}$) with the unique axis oriented along the internuclear dipolar vector. Finally, given that the dipolar tensor is both axially

symmetric and traceless, the three principal components of $\mathbf{D}$ are completely specified by the dipolar coupling constant, R_{DD} .

It is often convenient to express $\mathcal{H}_{DD}$ in spherical polar coordinates. Performing this transformation, the dipolar Hamiltonian can be rewritten as (14):

$$\hbar^{-1}\mathcal{H}_{DD} = R_{DD}[A + B + C + D + E + F] \quad (2.15)$$

where

$$A = -I_{Iz}I_{Sz}(3\cos^2\theta - 1) \quad (2.16)$$

$$B = \frac{1}{4}[I_{I+}I_{S-} + I_{I-}I_{S+}](3\cos^2\theta - 1) \quad (2.17)$$

$$C = -\frac{3}{2}[I_{Iz}I_{S+} + I_{I+}I_{Sz}]\sin\theta\cos\theta\exp(-i\phi) \quad (2.18)$$

$$D = -\frac{3}{2}[I_{Iz}I_{S-} + I_{I-}I_{Sz}]\sin\theta\cos\theta\exp(i\phi) \quad (2.19)$$

$$E = (-\frac{3}{4})I_{I+}I_{S+}\sin^2\theta\exp(-2i\phi) \quad (2.20)$$

$$F = (-\frac{3}{4})I_{I-}I_{S-}\sin^2\theta\exp(2i\phi) \quad (2.21)$$

The terms A to F are collectively referred to as the dipolar alphabet and the angles θ and ϕ orient the internuclear vector, $\mathbf{r}_{IS}$, in the laboratory frame of reference (Figure 2.4). Note that in the presence of a strong magnetic field where the Zeeman interaction is

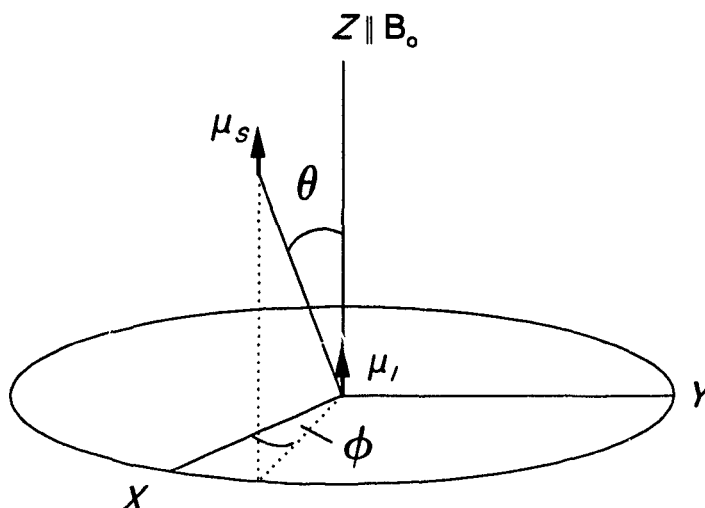


Figure 2.4 The orientation of the internuclear dipolar vector relative to the laboratory frame of reference is specified by the polar angles θ and ϕ .

much larger than the dipolar interaction, this Hamiltonian becomes truncated such that only terms A and B determine the NMR line shape (31). Furthermore, due to the presence of the "flip-flop operator" in term B , this component vanishes for heteronuclear spin pairs ($\gamma_I \neq \gamma_S$) but is non-zero for homonuclear spin pairs ($\gamma_I = \gamma_S$).

The secondary magnetic field experienced by nucleus I due to dipolar coupling with nucleus S will be a function of the spin state of S (*cf.* eq. 2.12). Thus, in the absence of anisotropic chemical shielding, the dipolar interaction causes an orientation-dependent splitting of the I resonance into $2S+1$ peaks, where S represents the spin quantum number of nucleus S . For a powder sample, all spatial orientations of the

internuclear dipolar vector are present relative to the external magnetic field so that each of the $2S + 1$ peaks in the NMR spectrum exists as a powder pattern. The resulting NMR spectrum for the case of two spin- $\frac{1}{2}$ nuclei is shown in Figure 2.5. This type of line shape is known as a "Pake doublet" after the physicist George Pake, who first observed this pattern in the proton spectrum of powdered $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (3).

In closing, it is apparent from the expression for R_{DD} , eq. 2.13, that the dipolar interaction is a function of the strength of the magnetic moments of the coupled nuclei as well as the spatial separation, r , between the coupled spins. This latter dependence can be exploited to derive valuable structural information. However, a word of caution

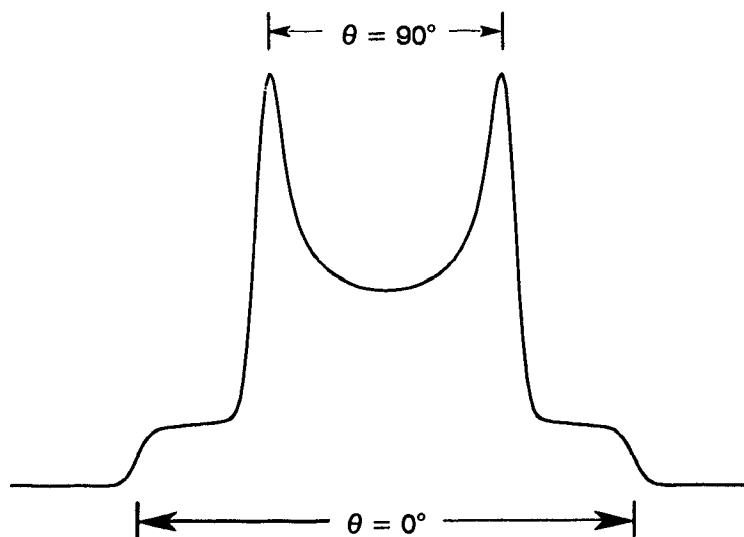


Figure 2.5 Powder spectrum arising solely from dipolar coupling between two spin- $\frac{1}{2}$ nuclei. The appearance of this spectrum is known as a Pake doublet.

is in order here in that the dipolar interaction is sensitive to motional averaging. In the presence of motional disorder, NMR derived bond lengths are too long when compared to the same data derived from diffraction experiments.

2.1.4 The Indirect Dipole-Dipole (J) Interaction

The indirect spin-spin interaction, also known as the J interaction, is conceptually similar to the direct dipolar interaction in that the source of the secondary magnetic field is a second nuclear spin. The difference lies in the method that this coupling is transmitted; the dipolar interaction is a *direct* "through-space" interaction while the J interaction is *indirectly* mediated *via* the intervening electrons in the electronic framework separating the coupled spins. The Hamiltonian describing this interaction between two spins, I and S , can be expressed as:

$$\hbar^{-1} \mathcal{H}_J = \mathbf{I}_I \cdot \mathbf{J} \cdot \mathbf{I}_S \quad (2.22)$$

where $\mathbf{J}$ is the indirect spin-spin coupling tensor. In general, $\mathbf{J}$ is a second-rank Cartesian tensor which is defined by nine independent elements. However, to first order, the antisymmetric component of $\mathbf{J}$ does not influence NMR peak positions (21) so that the above Hamiltonian can be expressed as:

$$\hbar^{-1} \mathcal{H}_J = J_{iso} \mathbf{I}_I \cdot \mathbf{I}_S + \mathbf{I}_I \cdot \mathbf{J}' \cdot \mathbf{I}_S \quad (2.23)$$

where $\mathbf{J}'$ is a symmetric, traceless tensor and J_{iso} is the isotropic value of the indirect spin-spin coupling. Neglecting antisymmetry, six independent elements are generally

required to define $\mathbf{J}$; with reference to the PAS, these are the three principal components, J_{ii} ($i=x,y,z$), as well as the Euler angles specifying the orientation of the PAS. In the presence of local symmetry, this number is reduced. The number of independent elements of $\mathbf{J}$ as a function of local point-group symmetry has been tabulated by Buckingham *et al.* (32, 33). The convention maintained in this thesis for the three principal components of $\mathbf{J}$ is: $|J_{zz}| \geq |J_{xx}| \geq |J_{yy}|$. The isotropic value of $\mathbf{J}$, observed in NMR spectra of fluids, is therefore given by $\frac{1}{3}(J_{zz} + J_{yy} + J_{xx})$. However, for the case of directly bonded nuclei, it is often assumed that $\mathbf{J}$ is also axially symmetric with the unique axis oriented along the chemical bond between the J -coupled spins. Under these approximations, $\mathbf{J}$ can be expressed in its PAS as follows:

$$\mathbf{J} = \begin{pmatrix} J_{\perp} & 0 & 0 \\ 0 & J_{\perp} & 0 \\ 0 & 0 & J_{\parallel} \end{pmatrix} = J_{iso} \cdot \mathbf{1} - \frac{\Delta J}{3} \cdot \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix} \quad (2.24)$$

where $\mathbf{1}$ is the unit tensor and ΔJ is the anisotropy in $\mathbf{J}$:

$$\Delta J = J_{\parallel} - J_{\perp} \quad (2.25)$$

Given the similar nature of the Hamiltonians governing the direct and indirect spin-spin interactions (eqs. 2.12 and 2.22, respectively) as well as the tensors which dictate the spatial dependence of these interactions (eqs. 2.14 and 2.24, respectively), it is not surprising that experimentally, one cannot separately observe these two distinct types of spin-spin coupling. That is, only the sum of these two interactions is manifested

in the NMR spectra of ordered systems so that an *effective* dipolar coupling is measured. The effective dipolar coupling constant, R_{eff} , is given by:

$$R_{eff} = R_{DD} - \frac{\Delta J}{3} \quad (2.26)$$

assuming an axially symmetric $\mathbf{J}$ tensor aligned with $\mathbf{D}$. Thus, it is clear that any experimental determination of $\mathbf{J}$ must involve an isolation from the effective coupling using prior knowledge of R_{DD} , the dipolar coupling constant. One consequence of this statement is that without information concerning the internuclear separation, r , between the coupled spins, it is not possible to obtain information concerning the anisotropy in $\mathbf{J}$. Although the simple manner in which both R_{DD} and the orientation of $\mathbf{D}$ are related to molecular structure is a tremendous advantage, accurate determinations of $\mathbf{J}$ remain a challenge. This topic will be dealt with in greater detail in Chapter 3. At this point, suffice it to say that precious little reliable experimental data is available concerning the anisotropic nature of $\mathbf{J}$. Thus, one of the most exciting aspects of this thesis involves the accurate measurement of two metal-phosphorus $\mathbf{J}$ tensors, both of which possess remarkably large anisotropies.

In concluding this section, it is worth mentioning that a non-relativistic theory of indirect spin-spin coupling was developed by Ramsey nearly half a century ago and is still used widely today (11). Qualitatively, the theory states that three different types of nucleus-electron interactions, commonly referred to as mechanisms, can mediate the transmission of nuclear spin information between two J -coupled nuclei. These are the orbital, spin-dipolar, and Fermi contact mechanisms. Traditionally, indirect spin-spin

couplings have been interpreted almost exclusively in terms of the Fermi contact mechanism. Since much of the discussion in Chapter 3 requires some familiarity with the Ramsey theory, particularly with the spatial dependence of each of these mechanisms, a more detailed discussion is provided in §2.3.2.

2.2 Measurement of Anisotropic Nuclear Spin Interactions

From the preceding discussions, it is apparent that the Zeeman interaction for a given nucleus in some arbitrary molecule can be perturbed *via* a complex network of secondary magnetic fields originating internally within the sample. Furthermore, this complexity is compounded by the fact that the strength of these secondary magnetic fields is, in general, a function of the orientation of the molecule in the external magnetic field. Thus, without intervening in any way, the solid-state NMR spectroscopist is generally presented with spectra that appear as featureless, broad humps. However, these unwanted "humps" contain embedded within them a wealth of valuable structural information and it is thus the spectroscopist's responsibility to select and employ whatever experimental techniques are available in order to recover the information of interest. Almost without exception, this will involve application of the standard high-power proton decoupling experiment, a method of eliminating the strong heteronuclear dipolar couplings involving the ubiquitous ^1H nucleus. Beyond this method, many of the remaining experiments in the arsenal of the spectroscopist involve rapid spinning of the sample about some axis relative to the external magnetic field. Often this angle is the "magic angle", 54.7° , which is referred to as the magic-angle-spinning (MAS) technique

(34, 35), a vital ingredient in the production of "high-resolution" NMR spectra of solid samples. However, given that the focus of this thesis is concerned with the anisotropic nature of the fundamental NMR interactions and not their orientational average, this class of experiments is not of major concern here. However, it is noteworthy that considerable effort has been expended by researchers in developing methods designed to "reconstruct" tensorial information from NMR spectra obtained under MAS conditions. For example, the Herzfeld-Berger approach (36) as well as the method of moments by Maricq and Waugh (37) can often be employed to obtain the three principal components of a chemical shift tensor, provided the tensor is incompletely averaged by MAS. As well, the recently introduced rotational-resonance magnetization-exchange experiment has attracted considerable interest for the ability to obtain homonuclear dipolar coupling information and consequently distance information under conditions of MAS (38).

The solid-state NMR techniques employed in this thesis for measuring anisotropic NMR interaction tensors have been dictated by the fact that not only are the magnitudes of the principal components of these tensors of fundamental importance and interest but also their orientations. In the absence of orientational information, a complete three-dimensional description of a given interaction tensor is not possible. Despite this fact, there is, in general, much more information available for the magnitudes of the principal components of these tensors than orientational data due to difficulties associated with experimentally characterizing tensor orientations. This can be readily appreciated if one considers as an example the measurement of a chemical shift tensor for a given nucleus in a molecule in the absence of other sources of internal magnetic fields. The solid-state

NMR spectrum for the case of a powder sample might look like that depicted in Figure 2.2, from which the three principal components of the chemical shift tensor can be readily extracted. However, information concerning the orientation of the PAS of the shift tensor is not available from such a spectrum. Obviously, in order to obtain this information from a given NMR technique, the experiment must provide a means of referencing the tensor PAS within the molecule of interest. In this thesis, two different experiments have been employed for this purpose. In Chapter 4, where anisotropic chemical shifts are the focus, an experiment known as the dipolar-chemical shift technique which utilizes powder samples has been used. However, in Chapter 3 where anisotropic spin-spin couplings are the primary concern, an experimental technique more reliable for this type of measurement, involving the use of single-crystal samples, has been applied.

2.2.1 Powder Samples

The powder spectrum arising from anisotropic chemical shielding of a nuclear spin, A , as well as dipolar coupling with a second nuclear spin, X , can be analyzed to obtain information concerning the orientation of the A -spin chemical shift tensor within the molecular frame of reference. This technique is known as the dipolar-chemical shift method (39, 40, 41). The referencing of the shift tensor PAS is provided "internally" by the fixed orientation of the AX dipolar tensor within the molecule. Although this experiment is attractive in that it uses powder samples which are generally readily obtained, the applicability is limited by the requirement for an isolated, dipolar-coupled

spin pair within the molecule of interest. This laboratory has written extensively on this technique in the process of characterizing numerous chemical shift tensors using a variety of isolated spin pairs (42, 43, 44). Therefore, another formal description is unnecessary here. Instead, the reader is referred to these articles for further details.

Although conventionally used in characterizing chemical shift tensors, it is noteworthy that the dipolar-chemical shift method has also been employed in the reverse sense for characterizing anisotropic spin-spin coupling tensors, particularly the anisotropy in $\mathbf{J}$ (*vide infra*). However, it is important to recognize that to do so inevitably requires assuming that $\mathbf{J}$ is axially symmetric and aligned with $\mathbf{D}$. Furthermore, unless dictated by symmetry, knowledge of the orientation of the chemical shift tensor for at least one of the coupled spins is prerequisite to the success of this approach. Given these drawbacks, it is clear that an experiment in which the $\mathbf{J}$ tensor is measured independently of the chemical shielding interaction is more desirable. The single-crystal NMR technique described below satisfies this requirement.

2.2.2 Single-Crystal Samples

In contrast with powder samples, where the probing of a given NMR interaction tensor by the external field is dictated by the nature of the sample, with single crystals this probing is controlled by the experimentalist. Although a variety of different approaches have been employed by researchers for characterizing NMR tensors with single-crystal samples, the method employed in this thesis is the conventional *orthogonal probe* experiment (45). This technique involves a sampling of the surface of an NMR

tensor in three arbitrary, yet orthogonal planes. The referencing of the tensor principal axis system to the molecular reference frame, essential in establishing orientation information, is provided "externally" in this experiment through X-ray crystallography. The major limitation lies in the requirement for a single crystal of suitable size, typically 2-3 mm on each side, although this criterion varies considerably with factors such as the nucleus being observed, relaxation times, *etc.* In the remainder of this section, a more formal description of the orthogonal probe experiment is provided. The mathematics of rotational transformations, of fundamental importance to this discussion, are briefly reviewed in Appendix I.

The single-crystal orthogonal probe experiment involves construction of a given NMR interaction tensor, λ , relative to some arbitrary reference frame, (x, y, z) , defined by the experimentalist which is then related to the molecular reference frame *via* X-ray crystallography. In this arbitrary reference frame, the symmetric part of λ can be expressed as:

$$\lambda = \begin{pmatrix} \lambda_{xx} & \lambda_{xy} & \lambda_{xz} \\ \lambda_{xy} & \lambda_{yy} & \lambda_{yz} \\ \lambda_{xz} & \lambda_{yz} & \lambda_{zz} \end{pmatrix} \quad (2.27)$$

The six independent elements of λ are determined by monitoring the magnitude of the interaction, λ_{obs} , upon rotation of the single crystal about each of the three axes of this reference frame. The variation in λ_{obs} as a function of rotation angle is referred to as a rotation pattern. Clearly, in order to interpret these rotation patterns, a description of

the orientation dependence of λ_{obs} relative to (x, y, z) is required. This is provided by the following expression:

$$\begin{aligned} \lambda_{obs} = & \lambda_{xx} \cos^2 \Phi_x + \lambda_{yy} \cos^2 \Phi_y + \lambda_{zz} \cos^2 \Phi_z + 2 \lambda_{xy} \cos \Phi_x \cos \Phi_y \\ & + 2 \lambda_{yz} \cos \Phi_y \cos \Phi_z + 2 \lambda_{xz} \cos \Phi_x \cos \Phi_z \end{aligned} \quad (2.28)$$

where $(\cos \Phi_x, \cos \Phi_y, \cos \Phi_z)$ represent the direction cosines of the external magnetic field vector with respect to (x, y, z) . Therefore, provided the direction cosines of the external magnetic field are known, eq. 2.28 can be used to fit the experimental rotation patterns. It is the results of these fits which are then used to construct λ with respect to this arbitrary frame of reference.

The manner in which the direction cosines of the external field are determined for a given rotation is conventionally represented as a series of rotational transformations, as illustrated in Figure 2.6. Each reference frame in this figure is defined by a right-handed Cartesian axis system (*cf.* Appendix I). The laboratory frame defines the direction of the external magnetic field, which is taken as the z axis. The goniometer frame is defined relative to the single-crystal NMR probe within which the single-crystal sample is placed. The goniometer of this probe contains a mechanism for rotating the single crystal about an axis perpendicular to the applied magnetic field direction. The single-crystal sample is mounted on a hollow, three-sided cube which is inserted in the probe goniometer. The axes of this cube define the cube frame, which is the arbitrary reference frame referred to in the preceding discussion within which λ is determined.

Laboratory Frame $\rightarrow$ Goniometer Frame. The transformation from the laboratory

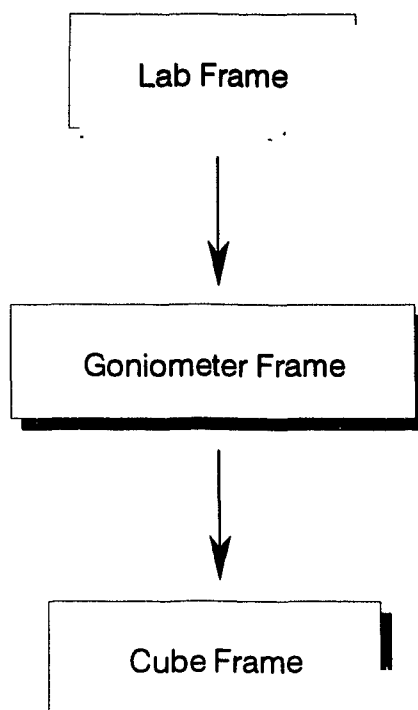


Figure 2.6 Diagram illustrating the rotational transformations involved in determining the direction cosines of the external field relative to the arbitrary reference frame in which λ is determined, known as the cube frame.

axis system to the probe goniometer reference frame is represented in Figure 2.7. Note that the rotation axis of the goniometer is z_{GON} which is oriented perpendicular to the external field direction (parallel to y_{LAB}). Also note that the rotation about z_{GON} has a right-handed sense in that the x axis is transformed to the y axis by this rotation. Clearly, the direction cosines of the external field in the goniometer frame will be a function of the rotation progress about z_{GON} , which is represented by ψ . Based on the Euler angles (*cf.* Appendix I) provided in Figure 2.7, the transformation of the external magnetic field vector into the goniometer reference frame is accomplished by:

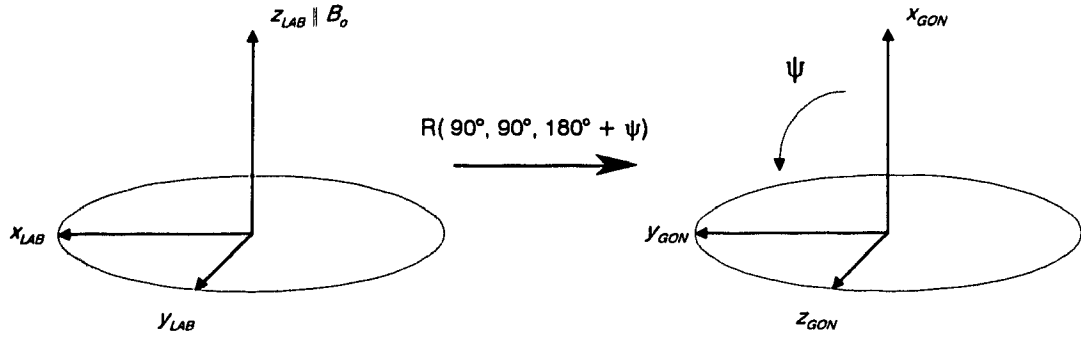


Figure 2.7 The transformation from the laboratory frame to the goniometer frame. The Euler angles, (α, β, γ) , describing this transformation are $(90^\circ, 90^\circ, 180^\circ + \psi)$, where ψ represents the angle of rotation about the goniometer rotation axis (z_{GON}).

$$(B_x \ B_y \ B_z)_{GON} = \begin{pmatrix} \sin \psi & 0 & \cos \psi \\ \cos \psi & 0 & -\sin \psi \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} B_x \\ B_y \\ B_z \end{pmatrix}_{LAB} \quad (2.29)$$

Since the external magnetic field direction is along the z axis in the laboratory frame, the direction cosines in the goniometer frame are given by $(\cos \psi, -\sin \psi, 0)$.

Goniometer Frame $\rightarrow$ Cube Frame. The NMR cube reference frame is defined by arbitrarily labelling each of the three axes of the cube holder, upon which the single-crystal sample is mounted, in a right-handed fashion (*cf.* Figure 2.8). Obviously, the direction cosines of the external field within this cube frame will depend upon the manner in which the cube is inserted in the probe goniometer. Thus, by inserting the cube in three different orientations, each corresponding to a different cube axis being parallel to the goniometer rotation axis, the surface of λ can be probed in three orthogonal planes. Note that it is extremely important when orienting the cube in the goniometer of the

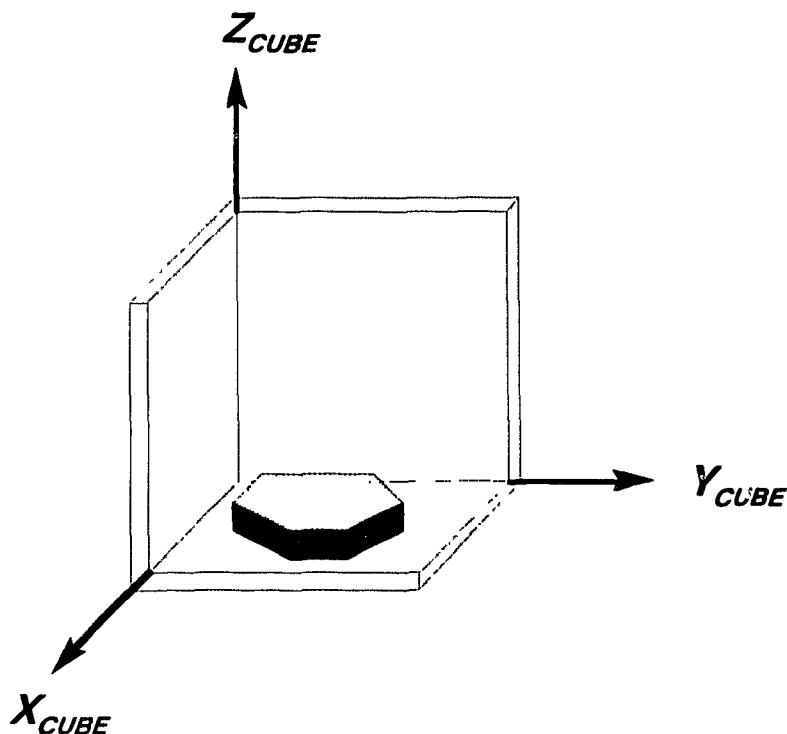


Figure 2.8 The single-crystal sample is mounted on a hollow, three-sided cube which is inserted in the probe goniometer. The cube reference frame is defined by arbitrarily labelling the cube axes in a right-handed fashion.

probe that a right-handed sense is maintained. For example, with the cube x axis aligned along the goniometer rotation axis, the cube y axis must be aligned with the external field direction and not the z axis. Similarly, the y rotation must start with the z axis of the cube aligned with the external field direction and the z rotation with the x axis of the cube parallel with the external field direction. The transformation of the magnetic field vector from the goniometer frame to the cube frame for rotation about the cube x axis, illustrated in Figure 2.9, can be represented as:

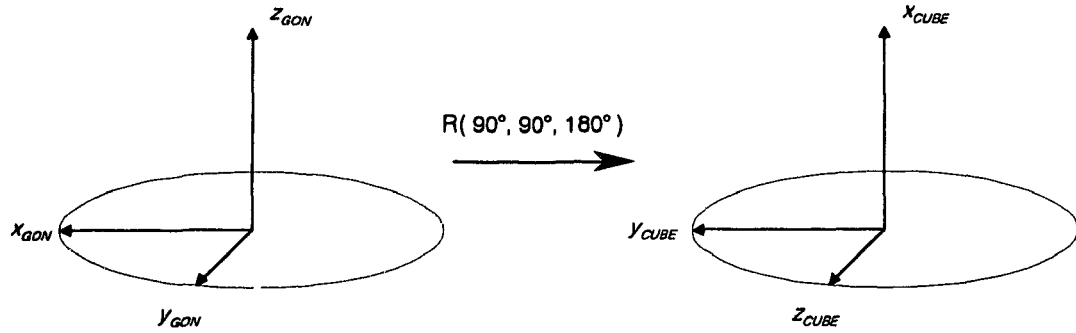


Figure 2.9 The transformation from the goniometer frame to the cube frame for one of the three orientations of the sample cube holder. For this rotation, the cube x axis is the rotation axis while the y axis is initially aligned along the external field direction.

$$(B_x \ B_y \ B_z)_{CUBE} = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} B_x \\ B_y \\ B_z \end{pmatrix}_{GON} \quad (2.30)$$

As the direction cosines of the external magnetic field relative to the goniometer frame are known (*cf.* eq. 2.29), relative to the cube frame these are determined to be $(0, \cos \psi, -\sin \psi)$. This information can then be used along with eq. 2.28 to derive an expression for the orientation dependence of λ_{obs} for rotation about the cube x axis:

$$\lambda_{obs} = \lambda_{yy} \cos^2 \psi + \lambda_{zz} \sin^2 \psi - 2 \lambda_{yz} \cos \psi \sin \psi \quad (2.31)$$

By making use of several trigonometric identities, this expression can be recast in the following form:

$$\lambda_{obs} = A_x + B_x \cos 2\psi + C_x \sin 2\psi \quad (2.32)$$

where:

$$\begin{aligned} A_x &= \frac{1}{2}(\lambda_{yy} + \lambda_{zz}) \\ B_x &= \frac{1}{2}(\lambda_{yy} - \lambda_{zz}) \\ C_x &= -\lambda_{yz} \end{aligned} \quad (2.33)$$

Thus, by performing a three-parameter linear least-squares fit of the observed rotation pattern, the three tensor elements λ_{yy} , λ_{zz} , and λ_{yz} can be determined from the magnitudes of the least-squares coefficients. In an analogous manner, the remaining tensor elements are obtained from fitting the rotation patterns measured for rotation about the cube y and z axes:

$$\begin{aligned} A_y &= \frac{1}{2}(\lambda_{xx} + \lambda_{zz}) & A_z &= \frac{1}{2}(\lambda_{xx} + \lambda_{yy}) \\ B_y &= \frac{1}{2}(\lambda_{zz} - \lambda_{xx}) & B_z &= \frac{1}{2}(\lambda_{xx} - \lambda_{yy}) \\ C_y &= -\lambda_{xz} & C_z &= -\lambda_{xy} \end{aligned} \quad (2.34)$$

The expressions for the six independent elements of λ relative to the cube reference frame can be derived from eqs. 2.33-2.34 as follows:

$$\begin{aligned} \lambda_{xx} &= \frac{1}{2}(A_y - B_y + A_z + B_z) & \lambda_{xy} &= \lambda_{yx} = -C_z \\ \lambda_{yy} &= \frac{1}{2}(A_z - B_z + A_x + B_x) & \lambda_{xz} &= \lambda_{zx} = -C_y \\ \lambda_{zz} &= \frac{1}{2}(A_x - B_x + A_y + B_y) & \lambda_{yz} &= \lambda_{zy} = -C_x \end{aligned} \quad (2.35)$$

If the three principal components of λ were the only information of interest to the experimentalist, the single-crystal experiment would essentially be complete at this point, the only remaining task being to diagonalize λ . The eigenvectors obtained from this procedure specify the orientation of the PAS of λ relative to the cube frame but clearly

this information alone is of no chemical significance. In order to determine the orientation of the PAS of λ relative to the molecular reference frame, it is necessary to perform two further transformations. These are schematically illustrated in Figure 2.10. The first transformation involves a rotation from the cube frame to the crystallographic axis system of the unit cell. The Euler angles specifying the rotation matrix used in this transformation are normally obtained by X-ray crystallography. Consequently, once the orientation of the PAS is known relative to the crystal frame, transformation into the molecular reference frame can be accomplished from the fractional coordinates of the

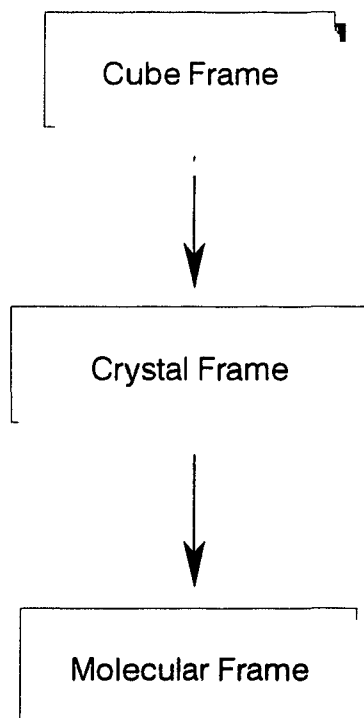


Figure 2.10 Diagram displaying the additional transformations required in order to determine the orientation of the principal axis system of λ relative to the molecular frame of reference.

unit cell. Clearly, this latter step is dependent upon the availability of a crystal structure for the sample under investigation.

Before concluding this discussion of the single-crystal orthogonal probe experiment, several further points are worth mentioning. The first is concerned with the problem of transforming the PAS of λ , which is orthogonal by nature, from the cube frame to a unit cell axis system which contains an oblique angle. This problem is relevant to Chapter 3 where two single-crystal samples have been investigated, both of which possess monoclinic unit cells ($\beta \neq 90^\circ$). In such cases, the unit cell axes as well as the fractional coordinates must be orthogonalized before transformation can be accomplished. For the monoclinic case, a small computer program has been written for this purpose. Note that the orthogonalized monoclinic reference frame is denoted as (a^* , b , c) or (a , b , c^*) depending upon whether the crystallographic a or c axis has been orthogonalized, respectively. The second point is that contrary to popular belief, the single-crystal experiment may not be capable of providing definitive information concerning tensor orientations relative to the molecular reference frame. Whenever the unit cell contains more than one magnetically distinct site, ambiguity arises in assigning the experimental tensors observed for these sites within the molecular frame of reference. This ambiguity can sometimes be removed by making use of angular dependent dipolar couplings associated with each site and/or local symmetry considerations (45). Note that two nuclei are magnetically distinct and thus possess non-coincident tensor orientations provided they are not related by a unit cell translation or an inversion center (17). The final point of note is that the rotation patterns measured in the orthogonal probe

experiment possess 2ψ periodicity, as is revealed by eq. 2.32. Consequently, rotations about a particular cube axis need only proceed from 0° to 180° in some fixed increment in order to define a rotation pattern.

2.3 Theoretical Interpretation of NMR Parameters

If the emphasis of this thesis was solely to experimentally characterize anisotropic NMR interactions, the background theory presented in §2.1 and §2.2 would be sufficient for this purpose. However, considerable emphasis has also been placed on interpretation of the experimental findings rather than simply cataloguing the data. In Chapter 4, where anisotropic carbon chemical shifts are the focus, this process has even involved a series of *ab initio* calculations of carbon chemical shielding tensors. In order to perform these tasks, some familiarity with the theory of the anisotropic interaction under investigation and its origins is required. This is the goal of the remainder of this section.

2.3.1 The Theory of Chemical Shielding

Consider first a closed-shell atom in an external magnetic field. According to Lamb (46), the presence of the external magnetic field induces the entire spherical electron cloud to precess freely about the external field direction. These electronic currents produce an induced magnetic field at the nucleus proportional and opposite in direction to the external magnetic field. Thus, the nucleus in a free atom is shielded by the electronic currents so that the effective field strength is less than the applied field strength; $\sigma > 0$. The magnitude of the total chemical shielding for a nucleus, A , in a

free atom with the origin of coordinates (gauge origin) at the nucleus is given by:

$$\sigma_A = \frac{\mu_o}{4\pi} \frac{e^2}{3m} \langle 0 | \sum_i \frac{1}{r_{iA}} | 0 \rangle \quad (2.36)$$

where μ_o is the permeability of free space, e and m are the electronic charge and mass, respectively, and r_{iA} is the distance from electron i to nucleus A . The summation is over all electrons, i . Clearly, the free-atom shielding term increases with the atomic number of the atom. For example, σ_A has been calculated to be 17.8 ppm for hydrogen and 260.7 ppm for the carbon atom (47).

When an atom becomes involved in a chemical bond as part of a molecule, the chemical shielding interaction is more complex. The presence of other nuclei hinders the flow of electronic currents in the molecule. Furthermore, the electron cloud in the local environment of a nucleus is no longer spherically symmetric so that the total chemical shielding depends upon the orientation of the molecule relative to the external magnetic field. This orientation dependence is described by the chemical shielding tensor, σ . Discussions of chemical shielding tensors in molecules are normally based on Ramsey's theory (10), in which the total shielding is somewhat arbitrarily separated into diamagnetic and paramagnetic contributions:

$$\sigma^{tot} = \sigma^d + \sigma^p \quad (2.37)$$

The individual tensor components for the diamagnetic and paramagnetic shielding terms for a nucleus, A , can be derived from the following expressions (48):

$$\sigma_{A\alpha\beta}^d = \frac{\mu_o}{4\pi} \frac{e^2}{2m} \langle 0 | \sum_i \frac{(\mathbf{r}_i \cdot \mathbf{r}_{iA} \delta_{\alpha\beta} - r_{iA} r_{iA\beta})}{r_{iA}^3} | 0 \rangle \quad (2.38)$$

$$\begin{aligned} \sigma_{A\alpha\beta}^p = -\frac{\mu_o}{4\pi} \frac{e^2}{2m^2} \sum_{k \neq 0} (E_k - E_0)^{-1} [& \langle 0 | \sum_i L_{i\alpha} | k \rangle \langle k | \sum_i \frac{L_{iA\beta}}{r_{iA}^3} | 0 \rangle + \\ & \langle 0 | \sum_i \frac{L_{iA\alpha}}{r_{iA}^3} | k \rangle \langle k | \sum_i L_{i\beta} | 0 \rangle] \end{aligned} \quad (2.39)$$

In the above expressions, α and β refer to the Cartesian components x , y or z , $\mathbf{r}_i$ and L_i are the position vector and orbital angular momentum operator, respectively, of electron i with respect to the gauge origin while $\mathbf{r}_{iA}$ and L_{iA} are with respect to the position of the nucleus, and $\delta_{\alpha\beta}$ is the Kronecker delta. Summations are taken over all electrons, i , and states, k , except the ground state ($k = 0$).

The diamagnetic shielding term is the molecular counterpart to the free-atom term (eq. 2.36). It yields a positive contribution to the total shielding. As well, due to the distance dependence of diamagnetic shielding, the core electrons of an atom make the largest contribution. Thus, relative to paramagnetic shielding, diamagnetic shielding varies little with the orientation of a molecule in the external magnetic field. Finally, it is relatively easy to calculate this term accurately as it depends only on the ground electronic state of the molecule. In fact, Flygare and Goodisman have provided a useful approximation to Ramsey's molecular diamagnetic term which is independent of the ground state wave function and, compared with *ab initio* calculations, gives reliable

results (49).

Paramagnetic currents in a molecule arise from the interaction between electrons possessing orbital angular momentum and the external magnetic field. These currents produce an induced magnetic field which is normally aligned parallel with the external magnetic field direction. Thus, the paramagnetic shielding contribution is normally negative and results in deshielding. Consequently, depending upon the relative magnitudes of σ^p and σ^d , the total shielding for a nucleus may be negative and therefore less than that for the bare nucleus. Note that the paramagnetic contribution is much more difficult to calculate accurately than the diamagnetic term due to a dependence on the wave functions and energies of the excited states of the molecule. Another important consideration is that it is predominantly the paramagnetic term that controls the variation in non-proton chemical shifts observed for a given nucleus within the variety of molecular environments in which it may reside. Thus, since interpretation of chemical shift trends is an important aspect of Chapter 4 of this thesis, a closer look at paramagnetic shielding and eq. 2.39 is warranted.

The paramagnetic shielding term can be visualized as the result of mixing of certain excited electronic states with the ground state in the presence of an external magnetic field. Which electronic states are involved in this mixing for a given molecular orientation is dictated by the requirement for nonzero matrix elements involving the orbital angular momentum operator in eq. 2.39. Thus, *s*-type orbitals do not contribute to paramagnetic shielding so that proton chemical shifts are controlled by the diamagnetic term. Another important consideration concerning these matrix elements is the symmetry

of the mixed states (50). Only mixing corresponding to magnetic-dipole-allowed transitions can contribute to the paramagnetic shielding term so that the mixing corresponds to a rotation of charge about the external field direction. This is illustrated more clearly in Figure 2.11, which shows how $\pi \leftrightarrow \sigma^*$ type mixing is of the proper symmetry and contributes to the paramagnetic term whereas $\pi \leftrightarrow \pi^*$ does not. This requirement of charge rotation can be related to the action of the orbital angular

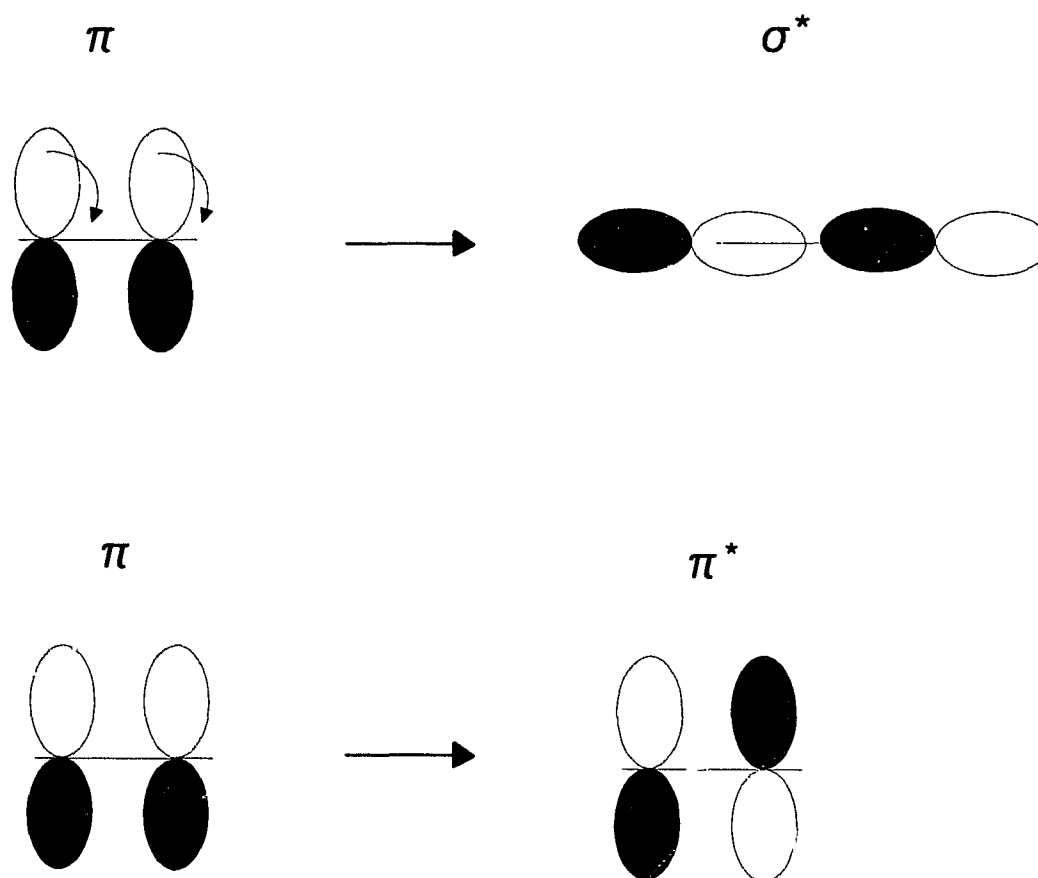


Figure 2.11 A transition such as $\pi \leftrightarrow \sigma^*$ involves a rotation of charge and thus contributes to the paramagnetic shielding term. However, $\pi \leftrightarrow \pi^*$ mixing is magnetic-dipole forbidden and therefore does not contribute.

momentum operator in eq. 2.39. The action of this operator on the various p - and d -type atomic orbitals has been previously tabulated by Jameson and Gutowsky (51). Two examples involving p -type atomic orbitals are illustrated in Figure 2.12; clearly the action

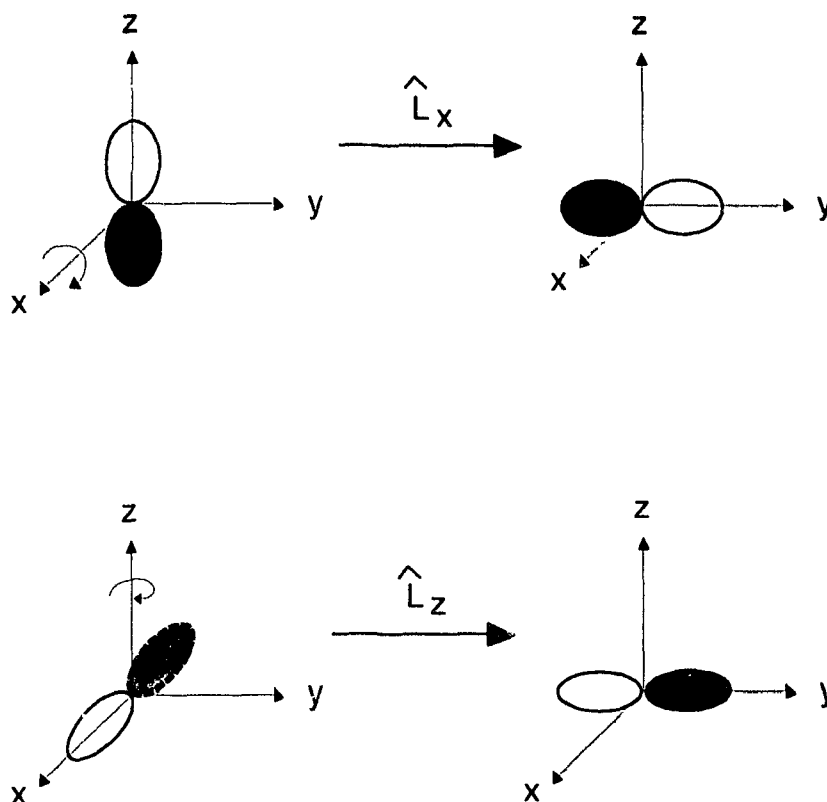


Figure 2.12 Two examples illustrating the "rotation of charge" action of the orbital angular momentum operator on p -type atomic orbitals. The effect of L_x on a p_z orbital is a transformation into a p_y orbital (top) while L_z operating on a p_x transforms it into a $-p_y$ orbital (bottom).

of L_i corresponds to a rotation about the i axis. Concepts such as these will be used extensively in Chapter 4 of this thesis.

Once the various modes of mixing have been identified based on angular

momentum and symmetry considerations, the relative contributions to the paramagnetic shielding are further governed by two "attenuation factors". One of these is the accessibility of the excited state involved, incorporated into eq. 2.39 through the $(\Delta E_k)^{-1} = (E_k - E_0)^{-1}$ factor. Thus, the smaller the energy gap from a ground state to a virtual singlet state of the molecule, the larger the contribution from this mode of mixing to the paramagnetic shielding term. Note that, in general, one cannot correlate paramagnetic shielding with a single electronic transition as many can contribute appreciably to this term. However, if the molecule has a low-lying virtual state such that one excitation is much lower in energy than the remainder, correlations of this nature become possible. The second factor is a distance consideration built into eq. 2.39 *via* matrix elements containing a r_{IA}^{-3} dependence. Intuitively, the more proximate a given charge rotation is to a nucleus, the stronger the nucleus will "feel" the effects of the induced magnetic field. In this regard, Mason has given a useful analogy in that the factor $\langle k | L r^{-3} | 0 \rangle$ in eq. 2.39 represents the transmission of the induced magnetic field to the nucleus which is at a distance r away (52).

In light of the complexity of the paramagnetic shielding interaction, reliable theoretical calculations of chemical shielding tensors are potentially of tremendous advantage in attempting to interpret experimental chemical shift tensor data. However, as indicated, calculation of the paramagnetic term using Ramsey's model is a difficult task. Furthermore, the total shielding is calculated as the sum of two large quantities opposite in sign and as such is subject to large errors. Early *ab initio* calculations of chemical shielding tensors were generally performed at the Hartree-Fock self-consistent-

field (SCF) level using coupled Hartree-Fock (CHF) perturbation theory (53) to treat the perturbation by the external magnetic field. However, normally a single gauge origin is employed (common-origin calculation), usually at the nucleus being studied, which can lead to gauge-dependent results depending upon the basis set employed and the size of the system treated. Qualitatively, this is due to the fact that contributions to the diamagnetic and paramagnetic terms are not calculated at the same level of accuracy with a change in gauge origin. Very large basis sets are required in order to deal with this problem and consequently, earlier shielding calculations were only practical for first row nuclei. However, within the last decade, significant improvements have been made with advances in computer technology and the advent of several variant schemes of the CHF method which apply gauge factors to atomic or localized molecular orbitals. The most common approaches are the *Gauge-Including Atomic Orbitals* (GIAO) approach (54), the *Individual Gauge for Localized Molecular Orbitals* (IGLO) method (55) as well as the *Localized Orbital-Local ORiGin* (LORG) approach (56). These latter two methods have the advantage that the shielding tensor is constructed as a sum of localized molecular orbital contributions, facilitating a chemical interpretation of the calculated data. Furthermore, within the past five years, several approaches for calculating shielding tensors have been developed based on higher levels of theory (57). Thus, it has now generally become possible to calculate reliable shielding tensors for nuclei of the first and second rows of the periodic table. Given the tremendous progress theoreticians have made in this area, programs for calculating shielding tensors are increasingly being used in experimental laboratories in order to better understand the relationship between

chemical shielding and electronic structure. This laboratory has advocated such an approach over the past several years and an example of the benefits obtained from this interplay between experiment and theory can be found in Chapter 4. For further details concerning theoretical calculations of chemical shieldings, the reader is referred to the text by Ando and Webb (48) as well as the review by Kowalewski and Laaksonen (58). The progress being made in this area is reviewed annually by C. J. Jameson in the Specialist Periodical Reports on Nuclear Magnetic Resonance (59).

2.3.2 The Theory of Indirect Spin-Spin Coupling

Nuclear spin-spin coupling *via* the intervening electrons can be visualized as a two-step process in which the magnetic moment of one of the coupled nuclei perturbs the electrons which in turn perturb the second nucleus. According to Ramsey (11), the non-relativistic Hamiltonian governing this coupling between two nuclear spins involves three different electron-nucleus interactions. These are the orbital, spin-dipolar, and Fermi contact interactions. The orbital term, which is conceptually similar to the chemical shielding interaction, describes the interaction between a nuclear spin with internal magnetic fields arising from induced electronic orbital motion. Unlike the case for shielding, however, where the induced electronic motion is due to the external magnetic field, it is the field originating from the coupled nuclear spin which is the source of the orbital mechanism. As for chemical shielding, the orbital term consists of a diamagnetic (OD) and paramagnetic (OP) contribution. The Fermi contact mechanism (FC) represents the interaction between a nuclear spin and electronic spin precisely at the

position of the nucleus. Finally, the spin-dipolar mechanism (SD) is a magnetic dipolar interaction between nuclear and electronic spin angular momenta. This latter term is similar to the FC mechanism but involves electrons at a finite distance from the nuclei. Using these Hamiltonians and second-order perturbation theory, the $\mathbf{J}$ tensor can be represented as the sum of OP-OP, SD-SD, FC-FC, and FC-SD interactions. As well, there is an OD contribution arising from first-order perturbation theory so that the total $\mathbf{J}$ tensor can be written as the sum of five terms:

$$\mathbf{J} = \mathbf{J}_{OD} + \mathbf{J}_{OP} + \mathbf{J}_{SD} + \mathbf{J}_{FC} + \mathbf{J}_{FC \times SD} \quad (2.40)$$

For two coupled nuclei, N and N' , the expressions for each of these terms are as follows (60):

$$\mathbf{J}_{OD} = \left(\frac{8m}{h} \right) \left(\frac{\mu_o}{4\pi} \right)^2 \mu_B^2 \gamma_N \gamma_{N'} \langle 0 | \sum_k \frac{\mathbf{r}_{kN} \cdot \mathbf{r}_{kN'}}{r_{kN}^3 r_{kN'}^3} | 0 \rangle \quad (2.41)$$

$$\begin{aligned} \mathbf{J}_{OP} = & \left(\frac{-2}{h} \right) \left(\frac{\mu_o}{4\pi} \right)^2 (2\mu_B \hbar)^2 \gamma_N \gamma_{N'} \sum_n (E_n^1 - E_0)^{-1} \langle 0 | \sum_k \frac{\mathbf{r}_{kN} \times \nabla_k}{r_{kN}^3} | n \rangle \\ & \times \langle n | \sum_j \frac{\mathbf{r}_{jN'} \times \nabla_j}{r_{jN'}^3} | 0 \rangle \end{aligned} \quad (2.42)$$

$$\begin{aligned} \mathbf{J}_{SD} = & \left(\frac{-2}{h} \right) \left(\frac{\mu_o}{4\pi} \right)^2 (2\mu_B \hbar)^2 \gamma_N \gamma_{N'} \sum_n (E_n^3 - E_0)^{-1} \\ & \times \langle 0 | \sum_k \frac{3(\mathbf{S}_k \cdot \mathbf{r}_{kN}) \mathbf{r}_{kN} - \mathbf{S}_k}{r_{kN}^3} | n \rangle \langle n | \sum_j \frac{3(\mathbf{S}_j \cdot \mathbf{r}_{jN'}) \mathbf{r}_{jN'} - \mathbf{S}_j}{r_{jN'}^3} | 0 \rangle \end{aligned} \quad (2.43)$$

$$\mathbf{J}_{FC} = \left(\frac{-2}{h}\right) \left(\frac{\mu_o}{4\pi}\right)^2 \left(\frac{16\pi\mu_B\hbar}{3}\right)^2 \gamma_N \gamma_{N'} \sum_n (E_n^3 - E_0)^{-1} \quad (2.44)$$

$$\times \langle 0 | \sum_k \delta(r_{kN}) \mathbf{S}_k | n \rangle \langle n | \sum_j \delta(r_{jN'}) \mathbf{S}_j | 0 \rangle$$

$$\mathbf{J}_{FC \times SD} = \left(\frac{-4}{h}\right) \left(\frac{\mu_o}{4\pi}\right)^2 \left(\frac{16\pi\mu_B\hbar}{3}\right)^2 (2\mu_B\hbar) \gamma_N \gamma_{N'} \sum_n (E_n^3 - E_0)^{-1} \quad (2.45)$$

$$\times \langle 0 | \sum_k \delta(r_{kN}) \mathbf{S}_k | n \rangle \langle n | \sum_j \left(\frac{(\mathbf{S}_j \cdot \mathbf{r}_{jN'}) \mathbf{r}_{jN'} - \mathbf{S}_j}{r_{jN'}^3} \right) | 0 \rangle$$

where μ_B is the Bohr magneton, $\mathbf{r}$ is the position vector of an electron, $\mathbf{S}$ is the electron spin operator, E^3 and E' are the energies of excited triplet and singlet states, respectively, and $\delta(r)$ is the Dirac delta function. All other symbols have their conventional meaning. Summations are taken over all electrons, k and j , and excited states, n . Since the orbital and SD contributions to $\mathbf{J}$ are antisymmetric, the total indirect spin-spin coupling tensor is, in general, antisymmetric. The FC contribution to the coupling, $\mathbf{J}_{FC}$, is completely isotropic whereas the cross term, $\mathbf{J}_{FC \times SD}$, is completely anisotropic and has a zero trace. The remaining terms can contribute to both the isotropic and anisotropic components of $\mathbf{J}$. Therefore, since $\mathbf{J}_{FC}$ is the only term that does not contribute to the anisotropy in $\mathbf{J}$, measurement of a large anisotropic $\mathbf{J}$ tensor is proof that mechanisms other than FC are important.

A relativistic analogue of the above theory, which combines each of Ramsey's electron-nucleus interactions into a single Hamiltonian, has been developed by Pyykkö

(61). However, it is possible to separate this relativistic Hamiltonian into two terms, one analogous to the FC interaction, depending on the electron density at the nuclei involved, and another incorporating the anisotropic interactions. Results from the application of this theory to J couplings involving heavier nuclei seem to indicate a general trend that relativistic effects lead to an increase in the anisotropy of J (62). Clearly, regardless of whether relativistic effects are important or not, measurement of an anisotropic J coupling is sufficient evidence for the importance of mechanisms other than FC.

As mentioned, indirect spin-spin couplings have traditionally been interpreted almost exclusively in terms of the FC mechanism. In order to facilitate such interpretations, a variety of approximations are frequently assumed in order to simplify Ramsey's expression (eq. 2.44). One of the most simplified, yet frequently invoked forms of this expression for two directly bonded nuclei, N and N' , is as follows:

$$J(N, N') = \left(\frac{\mu_o}{3\pi} \right)^2 \mu_B^2 h \gamma_N \gamma_{N'} ({}^3\Delta E)^{-1} |s_N(0)|^2 |s_{N'}(0)|^2 P_{s_N s_{N'}}^2 \quad (2.46)$$

where ${}^3\Delta E$ is an average triplet excitation energy, $|s_N(0)|$ is the magnitude of the valence s -electron density precisely at the nucleus, N , and $P_{s_N s_{N'}}$ is the N - N' bond order. Furthermore, for a related set of compounds, eq. 2.46 is often simplified even further to yield:

$$J(N, N') \propto k ({}^3\Delta E)^{-1} \alpha_N^2 \alpha_{N'}^2 |s_N(0)|^2 |s_{N'}(0)|^2 \quad (2.47)$$

where k is a constant for the compounds investigated and α_N represents the s -character

of the hybrid orbital used in transmitting nuclear spin information to N' . While these simple expressions appear to have some validity for C-H and C-C couplings, it must be emphasized that this is an extremely oversimplified approach. As will be discussed in Chapter 3 of this thesis, these simplistic ideas have even been applied in attempts to interpret metal-phosphorus coupling data!

The question of the relative importance of each of Ramsey's mechanisms remains of fundamental interest and significance. Many adaptations of Ramsey's theory of varying degrees of sophistication have been developed. Although Pople and Santry formulated a molecular orbital (MO) theory for the isotropic J coupling (63), Buckingham and Love were the first to consider the anisotropy in $\mathbf{J}$ (32). The results from these two classic papers indicate that the SD and orbital mechanisms are most important for coupling involving nuclei other than the proton and furthermore, only when there is multiple bonding between the coupled nuclei. As well, the anisotropy in $\mathbf{J}$ was predicted to be small for light nuclei such as ^1H , ^{13}C , and ^{19}F . However, later calculations provided examples contradicting these generalizations. For example, Blizzard and Santry found the orbital and SD contributions to be very important for some ^{19}F - ^{19}F and ^{19}F - ^{13}C couplings, despite an absence of multiple bonding (64). Similar conclusions were derived by Guest *et al.* (65) as well as Kowalewski *et al.* (66) for explaining geminal proton coupling trends within the series H_2O , NH_3 , and CH_4 . Although considerable progress has been made in the area of theoretical calculations of J couplings in recent years, reliable calculations are still generally limited to couplings involving first-row elements. Furthermore, much of the focus has centered on the

isotropic coupling constant only, where reliable experimental data is generally available, emphasizing the need for accurate experimental measurements of the anisotropy in $\mathbf{J}$. Thus, it is clear that the question of the relative importance of Ramsey's mechanisms to both the isotropic and anisotropic parts of $\mathbf{J}$ is still in the initial stages of being answered. However, in this light, a recent paper by Lazzeretti *et al.* has proposed an exciting idea in which electron current density maps could be used to visualize indirect spin-spin couplings and potentially elucidate the coupling mechanism(s) (67). For further details concerning the calculation of indirect spin-spin couplings, the reader is referred to review articles by Kowalewski (68) and Contreras and Facelli (69).

Chapter 3

Determination of a ^{199}Hg - ^{31}P $\mathbf{J}$ Tensor in a 1:1 and 1:2 Mercury-Phosphine Complex via Single-Crystal Phosphorus NMR Spectroscopy

3.1 Introduction

Although the literature abounds with investigations involving the application of *isotropic* indirect spin-spin (J) couplings to the study of molecular structure, there exists a profound lack of reliable data concerning the *anisotropic* nature of this interaction (32, 33, 70, 71). As was pointed out in §2.1.4, the experimentalist is confronted with an inherent obstacle in measuring accurate $\mathbf{J}$ tensors in that the anisotropic component of the J coupling is physically inseparable from the direct dipolar coupling (30, 39, 40, 42). From a theoretical standpoint, we have also seen in §2.3 the problems associated with the computation of $\mathbf{J}$ tensors and the difficulty in assessing the reliability of the data available. This situation contrasts sharply with that for the better understood chemical shielding interaction where the compilation of accurate experimental shielding tensor data over the past two decades has provided benchmarks for theoreticians to facilitate the development of the powerful computer code now available for calculating shielding tensors. A comparable understanding of the indirect spin-spin coupling interaction would also be facilitated by such a harmonious relationship between experiment and theory. The common tendency to assume FC dominance when calculating and/or interpreting J couplings is an axiom that has propagated due to a lack of $\mathbf{J}$ tensor information and needs to be substantiated. The research described in this chapter illustrates an attempt to

promote this theme, providing the most reliable experimental measurements of anisotropic **J** tensors to date.

Several NMR spectroscopic approaches have been adopted in the past for acquiring **J** tensor information. A common method involves NMR studies of solute molecules oriented in liquid crystalline solvents (72, 73). Unfortunately, the analysis of such spectra is compounded by the need to determine the orientational order tensor as well as suitable vibrational corrections to the experimental coupling tensor. Furthermore, significant experimental error can be introduced when using X-ray crystallographic data to determine the dipolar interaction contribution as the molecular geometry can depend upon both the liquid crystal solvent as well as the orientation of the solute molecules within the liquid crystalline matrix (74). For example, Jokisaari *et al.* have measured the anisotropy in the one-bond ^{19}F - ^{13}C **J** tensor of methyl fluoride ($J_{iso} = -161$ Hz) in the conventional manner using nine different liquid crystal solvents and found anisotropies ranging from 50 Hz to -5000 Hz (74a)! A more robust approach involves the analysis of solid-state NMR spectra of slow MAS (41) or, preferably, static powder samples (39, 40, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86). However, as indicated in §2.2.1, such investigations are also potentially problematic due to a general dependence upon a multitude of parameters. There has also been considerable recent interest in extracting information concerning the anisotropy in the **J** tensor from the magnitudes of residual dipolar couplings observed in MAS spectra of spin- $1/2$ nuclei that are spin-spin coupled to a quadrupolar nucleus which experiences a non-zero electric field gradient (87). Unfortunately, the magnitude of this residual coupling is again a function

of numerous parameters, the most problematic often being the quadrupolar coupling tensor at the quadrupolar nucleus. Once again, particularly in systems of low site symmetry, one is forced to make several assumptions which heighten the experimental uncertainty associated with the derived values of ΔI .

A superior approach for the experimental characterization of indirect spin-spin coupling tensors is the single-crystal NMR technique. The key to the success of this powerful method lies in the fact that for multiple-interaction spin systems, analysis of the coupling data is completely independent of the chemical shift interaction, thereby eliminating assumptions inherent in the aforementioned approaches. Despite this advantage, it is surprising that, to date, there have only been four single-crystal studies claiming the elucidation of an anisotropic $\mathbf{J}$ tensor (88, 89, 90). Furthermore, one of these, a classic paper in this area involving a study of $^1J(^{31}\text{P}, ^{31}\text{P})$ in tetraethyldiphosphine disulfide (TEPS) (89a), has recently been shown to be flawed (91). The anisotropy in $^1J(^{31}\text{P}, ^{31}\text{P})$ in TEPS, originally thought to be on the order of 2 kHz, instead was revealed to be negligibly small! As well, this study also calls into question the reports of an anisotropic ^{31}P - ^{31}P $\mathbf{J}$ tensor in a related molecule, tetrabutylidiphosphine disulfide (89b).

Given the importance of characterizing the $\mathbf{J}$ tensor rather than simply its trace as well as the paucity of reliable experimental data in this field, this lab has initiated a series of investigations into a variety of metal-phosphorus $\mathbf{J}$ tensors using solid-state NMR studies of powder samples (80, 82, 83, 84, 86). This chapter outlines the first attempts to employ the more powerful single-crystal experiment to characterize metal-phosphorus $\mathbf{J}$ tensors. Specifically, the ^{199}Hg - ^{31}P one-bond indirect spin-spin coupling

tensor has been investigated in two complexes of the general type $\text{Hg}(\text{X})_2(\text{PR}_3)_n$. Such $\text{Hg}(\text{II})$ species have been extensively investigated using ^{31}P solution NMR and a large amount of data has been compiled for the isotropic value of the ^{199}Hg - ^{31}P $\mathbf{J}$ tensor (92). Values of $^1J(^{199}\text{Hg}, ^{31}\text{P})_{\text{iso}}$, which span a range on the order of 17 kHz (93), have been found to be an extremely sensitive function of molecular structure and have been correlated with numerous structural parameters such as Hg-P bond lengths, various bond angles, and the number of phosphine ligands (93, 94). Analogous empirical relationships between $J(\text{M}, ^{31}\text{P})_{\text{iso}}$ and molecular structure can be found for complexes containing other NMR-active metals such as $^{111/113}\text{Cd}$ and ^{195}Pt (93, 94, 95, 96). Of particular relevance to the present study is the fact that for a given phosphine and anion, the magnitude of $^1J(^{199}\text{Hg}, ^{31}\text{P})_{\text{iso}}$ decreases by 30-50% with increasing n , the number of phosphine ligands coordinated to mercury (92a, b, c, d). Interpretation of this general observation invariably involves arguments which only consider the FC mechanism. For example, when $n = 1$ (1:1 complex), the majority of these species exist as dimers in solution and the larger values of $^1J(^{199}\text{Hg}, ^{31}\text{P})_{\text{iso}}$ are thought to be the result of a greater electron-deficiency at the Hg atom which results in stronger Hg-P σ -bonding interactions (92a). Stronger σ -bonding implies greater "s-character" and hence an FC-dominated J coupling is expected to increase. However, in light of the findings obtained previously from powder studies of several 1:1 complexes (80, 83), which proposed large anisotropic $\mathbf{J}$ tensors, it would appear that other mechanisms are involved and that these traditional arguments may not be completely valid.

In an effort to characterize more fully the ^{199}Hg - ^{31}P indirect spin-spin coupling in

these species by examining the tensor rather than simply the isotropic value, phosphorus single-crystal NMR studies have been performed for both a 1:1 complex, $\text{HgPCy}_3(\text{NO}_3)_2$ (Cy = cyclohexyl) (**1**), and a 1:2 complex, $\text{Hg}(\text{PPh}_3)_2(\text{NO}_3)_2$ (Ph=phenyl) (**2**). This study represents the first determination of a ^{199}Hg - ^{31}P **J** tensor in a 1:2 species. There are several inherent advantages to using such systems for the determination of **J** tensors, thereby imparting a greater degree of confidence into the results. For example, the long Hg-P bond lengths (*ca.* 2.38 Å) result in small direct dipolar contributions to the observed couplings (*ca.* 650 Hz) while evidence indicates that the anisotropic **J** component is large (80, 83). This combination of a small dipolar coupling constant and a possible large anisotropy in **J** is in contrast with many of the earlier studies, where the direct dipolar coupling contribution was dominant. Systems of the latter type are in general undesirable as the effective dipolar coupling is often smaller than the calculated dipolar coupling. This makes it difficult to assess whether an anisotropic **J** tensor or motional averaging is responsible for the reduction in the effective coupling. Furthermore, the bulky nature of the mercury-phosphines should help to attenuate any effects of motional averaging. Finally, the large magnitude of the isotropic *J* coupling (8.2 kHz for **1** and 5.6 kHz for **2**) ensures that the ^{199}Hg satellites, observed in the ^{31}P single-crystal NMR spectra due to spin-spin coupling with ^{199}Hg nuclei (natural abundance 16.84%), are well-separated from the central, uncoupled phosphorus peak(s). The remainder of this chapter is organized as follows. In §3.2, experimental details will be provided. In §3.3, the ^{31}P single-crystal NMR spectra observed for **1** and **2** will be discussed and interpreted in terms of the solid-state structures of these species. Section

3.4 will be devoted to an analysis of the phosphorus chemical shielding tensors in **1** and **2** as well as the two-bond ^{31}P - ^{31}P spin-spin coupling in **2**. The main emphasis of the chapter will be in §3.5 where the analysis and results for the ^{199}Hg - ^{31}P **J** tensors will be presented. Finally, some concluding remarks will be provided in §3.6.

3.2 Experimental Section

Compound Preparation. Dinitrato(tricyclohexylphosphine)-mercury(II), **1**, was prepared by a standard synthetic procedure as described elsewhere (92*b*). Dinitrato-bis(triphenylphosphine)-mercury(II), **2**, was also prepared according to a previously described synthetic procedure (97). The purity of these complexes was verified by solution ^{31}P NMR studies. The large single crystals used in the NMR studies were obtained from a dichloromethane solution by slowly evaporating the solvent over the course of a month. The remaining crystals were subsequently ground and used for the acquisition of the spectra obtained for powdered samples of **1** and **2**.

X-ray Crystallography. Single crystals of approximate dimensions $3.5 \times 3.0 \times 1.0$ mm for **1** and $4.0 \times 3.0 \times 2.0$ mm for **2** were mounted on hollow, three-sided alumina cubes with axes 4 mm in length. NMR cube reference frames were defined by arbitrarily labelling the cube axes *X*, *Y*, *Z* in a right-handed fashion. Orientation matrices describing the location of the monoclinic unit cell axes with respect to these reference frames were obtained by placing the NMR samples in the alumina cube holders on an X-ray diffractometer and indexing 21 well-centered reflections for **1** and 29 well-centered reflections for **2**. Errors in the position of each axis were estimated to be less than 0.5° .

The Euler angles describing the orientation of the orthogonalized monoclinic crystallographic axis system (a^* , b , c) of **1** with respect to its NMR cube reference frame were determined to be $\alpha = 357.5^\circ$, $\beta = 90.6^\circ$, and $\gamma = 178.1^\circ$. For the case of **2**, these angles were determined to be $\alpha = 310.6^\circ$, $\beta = 93.8^\circ$, and $\gamma = 5.9^\circ$ (a , b , c^*) with respect to the NMR cube frame). The monoclinic unit cell parameters for **2** were determined as follows: $a = 13.384(8) \text{ \AA}$, $b = 13.994(7) \text{ \AA}$, $c = 17.864(8) \text{ \AA}$, and $\beta = 91.54(4)^\circ$, which are in good agreement with the unit cell reported in the X-ray crystallographic study of Buergi *et al* (92f).

Solid-State NMR. Single-crystal ^{31}P NMR spectra were acquired at 81.03 MHz (4.7 T) on a Bruker MSL-200 spectrometer using a single-crystal goniometer probe from Doty Scientific. Rotation patterns were obtained by rotating the crystal about each of the three orthogonal cube axes within a hollow cubic receptacle in the probe goniometer, with the rotation axis oriented perpendicular to the external field direction. For **1**, spectra were obtained for a total of 16 orientations for each rotation pattern, corresponding to rotations from 0° to 90° in 9° increments and from 90° to 180° in 18° increments. For **2**, spectra were obtained in 9° increments from 0° to 180° , resulting in the acquisition of 21 spectra for each of the three rotation patterns. The origin of the increased interval size within the latter half of each rotation pattern for **1** was due to the excessive time required to obtain the NMR data; the total spectrometer time necessary to complete the single-crystal NMR experimentation was approximately 21 days. This difficulty was, in turn, related to the long proton spin-lattice relaxation times in **1** as well as the need to obtain adequate signal-to-noise ratios in order to define the resonance

frequencies of the weak ^{199}Hg satellite peaks. For each orientation of the single crystal of **1**, typically 32 free-induction-decays (fids) were signal averaged with a recycle delay of 20 min. For **2**, typically 80 fids were acquired using a 5 min recycle delay. In order to extract accurate peak positions from the complex ^{31}P single-crystal NMR spectra of **2**, the multiplets were deconvoluted with Gaussian peaks using the Bruker software package WINFIT.

^{31}P NMR spectra were also obtained at 4.7 T for powdered samples of **1** and **2** as well as with a Bruker AMX-400 NMR spectrometer (9.4 T) operating at a ^{31}P Larmor frequency of 161.98 MHz. Bruker double-air-bearing MAS probes were employed at both fields with the powdered samples packed into zirconium oxide rotors of outer diameter 7 mm (4.7 T) and 4 mm (9.4 T). Experiments involving rotation of the single crystal of **1** at the magic angle were also obtained in this fashion.

All ^{31}P NMR spectra were obtained by employing the FLIPBACK pulse sequence (98) under conditions of cross-polarization and high-power proton decoupling. Proton 90° pulse widths of $3.45\ \mu\text{s}$ and $3.95\ \mu\text{s}$ were used for the single-crystal and powder spectra, respectively. In all cases, a cross-polarization time of 5 ms was employed. Spectra have been referenced with respect to 85% H_3PO_4 (aq) which, for the acquisition of spectra for powdered samples, involved setting the isotropic peak observed in the MAS spectrum of $\text{NH}_4\text{H}_2\text{PO}_4$ to 0.8 ppm.

NMR Line Shape Calculations. Calculation of the ^{31}P NMR line shapes obtained for static powder samples of **1** and **2** were performed on a 486 personal computer using simulation software developed in this laboratory. For the case of **1**, the program *SOLIDS*

(44) was employed. However, for the more demanding case of **2**, an independent program was developed using the C language. A listing of this computer code is provided in Appendix II. In all cases, powder averaging was accomplished *via* the POWDER routine of Alderman *et al.* (99).

3.3 Phosphorus Single-Crystal NMR Spectra

The purpose of this section is to discuss how the ^{31}P single-crystal NMR spectra obtained for **1** and **2** are interpreted in terms of both the crystallographic and molecular structures of these species. Particular emphasis is placed upon derivation of the number of magnetically distinct phosphorus sites as a function of the crystallographic space group symmetry. This task is a crucial ingredient to the analysis of single-crystal NMR data and, furthermore, illustrates the importance of the solid-state crystal structure to this experiment.

3.3.1 The 1:1 Mercury-Phosphine Complex

Previous X-ray diffraction analyses of 1:1 mercury-phosphine complexes have shown that these molecules crystallize either as distinct centrosymmetric dimers or as polymeric chains (100). One of these earlier studies involved $[\text{HgPCy}_3(\text{NO}_3)_2]_2$, where the centrosymmetric dimeric structure was found (100). However, in light of the apparent structural polymorphism observed for these 1:1 species, an X-ray structure was obtained for **1** using a tiny crystal obtained from the larger single crystal used in the NMR study, revealing the polymeric chain structure. For further details concerning the

X-ray crystallographic aspects of this study, the reader is referred to reference 101. A picture of the unit cell of **1**, monoclinic space group $P2_1/c$ (#14), is provided in Figure 3.1.

As illustrated in Figure 3.1, the unit cell of **1** contains four crystallographically equivalent phosphorus nuclei. Each pair of phosphorus nuclei related by either a 2_1 axis or a c glide plane is magnetically non-equivalent in the NMR experiment (17). However, the remaining two possible pairs consist of magnetically equivalent ^{31}P nuclei due to the

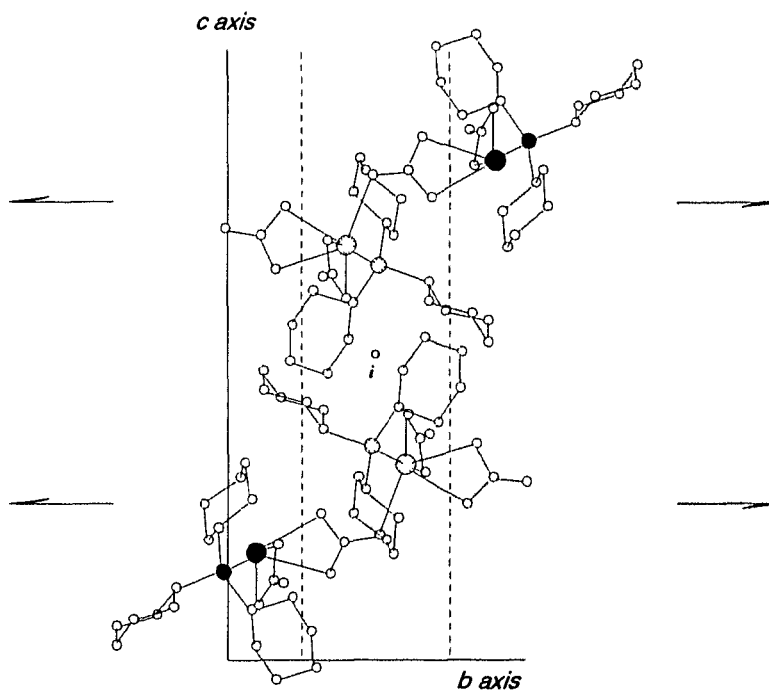


Figure 3.1 The unit cell of **1**, projected into the crystallographic *bc* plane. The pertinent space group symmetry elements are also shown. The two magnetically distinct Hg, P spin pairs are indicated by dotted and closed circles for sites 1 and 2, respectively. Hydrogen atoms have been omitted for clarity.

presence of an inversion centre. Consequently, for a general orientation of a single crystal of **1** in an external magnetic field, peaks from two magnetically distinct sites (arbitrarily designated sites 1 and 2 in Figure 3.1) are observed. This is illustrated in Figure 3.2, which shows the ^{31}P single-crystal NMR spectrum obtained for rotation about the cube *X* axis at the 81° orientation. For each site, a total of three peaks are obtained; a strong central peak due to ^{31}P nuclei that are adjacent to mercury isotopes with spin $I = 0$ and two much weaker satellite peaks resulting from ^{31}P nuclei that are spin-spin

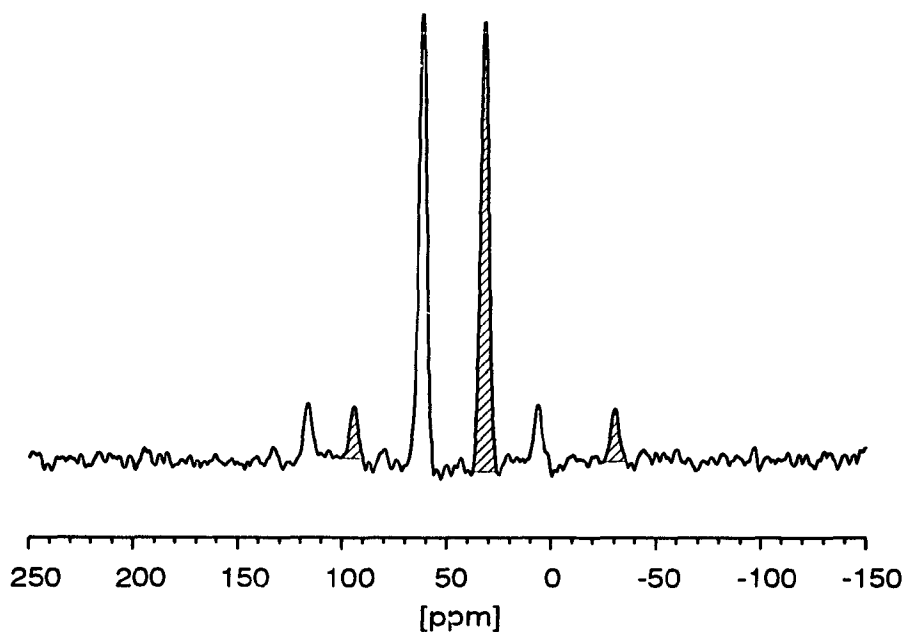


Figure 3.2 A representative ^{31}P single-crystal NMR spectrum obtained for the $X(81^\circ)$ orientation of the single crystal of **1** in the external magnetic field. Peaks arising from the two magnetically non-equivalent phosphorus sites have been distinguished by open and dashed lines for sites 1 and 2, respectively.

coupled to ^{199}Hg nuclei ($I = 1/2$, natural abundance = 16.84%). Although the mercury isotope ^{201}Hg also possesses a non-zero spin angular momentum ($I = 3/2$, natural abundance = 13.22%), no evidence of ^{201}Hg - ^{31}P spin-spin coupling was apparent in the single-crystal ^{31}P NMR spectra. The variation in resonance frequency of the uncoupled ^{31}P peaks or, equivalently, the average frequencies of the ^{199}Hg satellite peaks with orientation of the single crystal in the external magnetic field can be analyzed to obtain phosphorus chemical shift (CS) tensor information (*cf.* §3.4.1 *vide infra*). Similarly, the orientation dependence of the **splittings** of the satellite peaks can be analyzed, independent of the CS interaction, to obtain the sum of the ^{199}Hg - ^{31}P direct and indirect spin-spin coupling tensors (*cf.* §3.5.1 *vide infra*).

3.3.2 The 1:2 Mercury-Phosphine Complex

A picture of the unit cell of **2**, monoclinic space group $C2/c$ (#15), is shown in Figure 3.3. The unit cell contains four crystallographically equivalent molecules (92f). The mercury atom of each molecule is positioned on a crystallographic two-fold rotation axis relating the two phosphine ligands and the two nitrate groups within each molecule. Although the two phosphorus nuclei within a molecule are crystallographically equivalent and therefore possess CS tensors with identical principal components and isotropic chemical shifts, these nuclei are magnetically distinct as the two-fold rotation symmetry is not sufficient to constrain the orientations of the phosphorus CS tensors to be coincident (17). Consequently, the two phosphorus nuclei constitute a general dipolar-coupled homonuclear AB spin system. Furthermore, consideration of the crystallographic

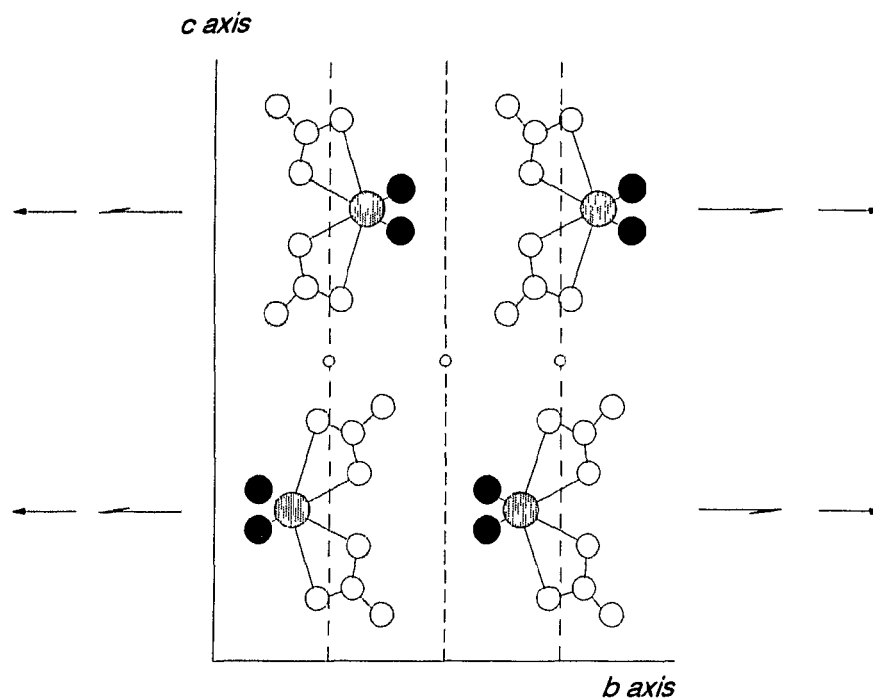


Figure 3.3 The unit cell of **2**, projected into the crystallographic *bc* plane. The pertinent space group symmetry elements are also shown. Mercury atoms are indicated by dotted circles while phosphorus atoms are indicated by closed circles. Phenyl rings have been omitted for clarity.

symmetry reveals that these phosphorus homonuclear spin pairs within different molecules are indistinguishable and consequently, for a general orientation of the single crystal of **2** in an external magnetic field, NMR peaks are observed for two distinct phosphorus sites.

Despite the fact that the ^{31}P single-crystal NMR spectra for both **1** and **2** exhibit peaks from two magnetically distinct sites, the spectra obtained for **2** are, in general, more complex due to the additional influence of homonuclear phosphorus spin-spin

coupling. The homonuclear direct dipolar coupling constant, $R(^{31}\text{P}, ^{31}\text{P})$, is calculated to be 220 Hz, based on a P-P intramolecular separation of 4.474 Å in **2** (92f). As well, Wu and Wasylishen have measured $^2J(^{31}\text{P}, ^{31}\text{P})_{iso}$ to be 250 Hz (102). Both the CS difference between the two ^{31}P nuclei and the homonuclear spin-spin coupling interaction change as the single crystal is rotated in the external magnetic field as the chemical shielding and spin-spin interactions are anisotropic in nature. Consequently, for a general orientation of the single crystal of **2**, one can, in principle, observe A_2 , AB , or AX patterns in the ^{31}P NMR spectra arising from this homonuclear two-spin system (Figure 3.4). Griffin and co-workers, who examined carbon-13 NMR spectra of a single crystal of diammonium oxalate- $^{13}\text{C}_2$ monohydrate, have reported the only other example of this phenomenon in single-crystal NMR spectra (103). For homonuclear spin pairs in static powder samples, where a statistical distribution of molecular orientations relative to the external magnetic field is present, the presence of individual A_2 , AB , or AX spectra (40) has been found to produce complex powder pattern line shapes (104, 105). The equations governing the peak positions and intensities of the four transitions arising from a homonuclear spin pair (40, 103) are provided in Appendix II.

Another interesting feature apparent in the ^{31}P single-crystal NMR spectra of **2** is the appearance of the mercury-199 satellite peaks. These peaks constitute the AB part of an ABX spin system. As mentioned in §3.3.1, the anisotropy in the splittings of the ^{199}Hg satellites can be analyzed to obtain the ^{199}Hg - ^{31}P spin-spin coupling tensors, independent of the ^{31}P CS interaction and, in the case of **2**, the ^{31}P - ^{31}P spin-spin coupling. From Figure 3.4, it is clear that the appearance of the ^{199}Hg sub-spectra can exhibit a

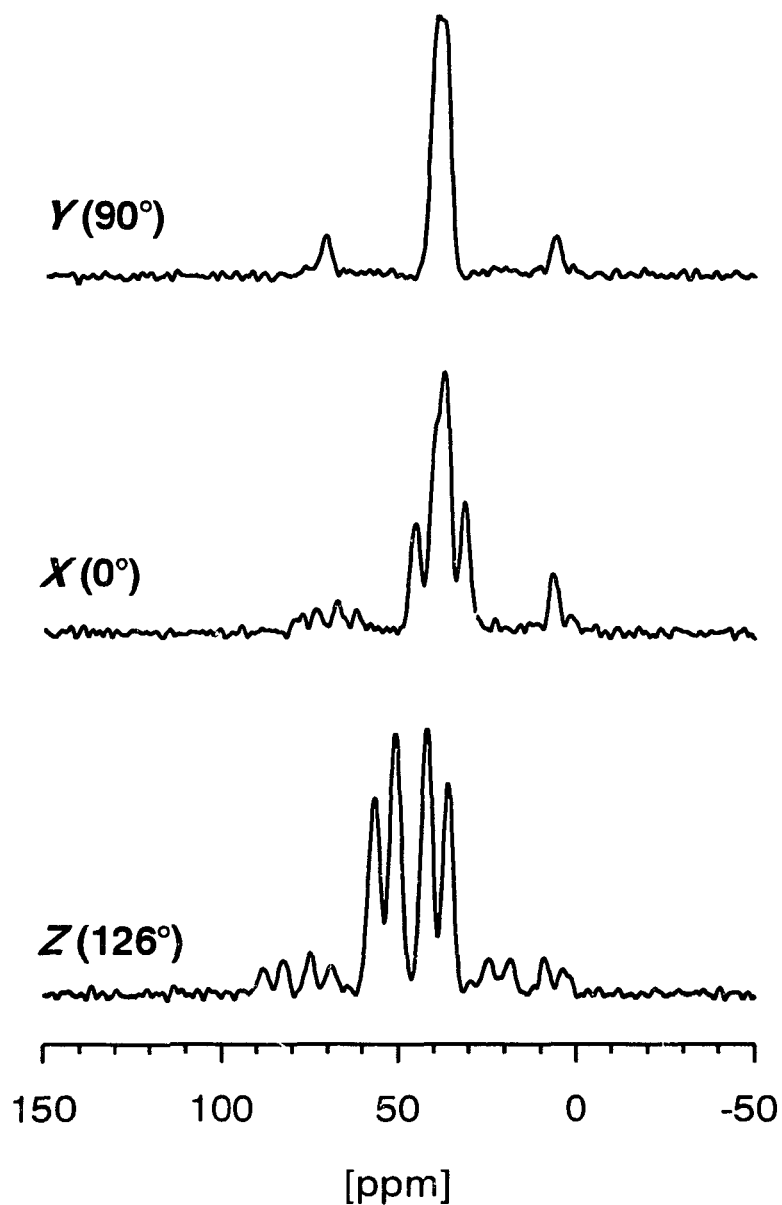


Figure 3.4 Typical ^{31}P single-crystal NMR spectra obtained for **2** at an external magnetic field strength of 4.7 T. The variation in line shape of the central, intense peaks is due to changes in the relative sizes of the chemical shift difference between the two phosphorus nuclei and the homonuclear ^{31}P - ^{31}P spin-spin coupling as a function of the orientation of the single crystal. Thus, these spectra can exhibit predominantly A_2 (upper), AB (middle), or AX (bottom) character as the single crystal is rotated.

strong dependence on the spin state of the ^{199}Hg nucleus, $m = \pm 1/2$. This asymmetric behaviour is most evident at orientations where the ^{31}P , ^{31}P homonuclear spin pair is tightly coupled. The origin of this asymmetry lies in the fact that for a general orientation of the single crystal relative to the external magnetic field, the two ^{31}P nuclei of the *ABX* spin system experience a modified CS difference due to spin-spin coupling with ^{199}Hg . This modified CS difference is a function of the spin state of the ^{199}Hg nucleus and, qualitatively, arises due to the fact that the two ^{199}Hg - ^{31}P spin-spin coupling tensors are not coincident. Note that the asymmetry in the satellite peaks is a function of the ^{199}Hg - ^{31}P direct dipolar and *anisotropic J* coupling only. If the ^{199}Hg - ^{31}P spin-spin coupling interaction consisted of purely isotropic *J* coupling, identical ^{199}Hg sub-spectra would be anticipated for any orientation of the single crystal in the external magnetic field. Finally, asymmetric ^{199}Hg satellite peaks have also been observed in ^{31}P MAS spectra of **2** at slow spinning speeds, the origin of which is qualitatively analogous to that observed in the present study (106).

3.4 Phosphorus Nuclei Not Coupled to Mercury-199

Although the main focus of this chapter involves the measurement of the ^{199}Hg - ^{31}P *J* tensors in **1** and **2**, it should be emphasized that valuable information is available from an analysis of the central peaks in the single-crystal spectra due to ^{31}P nuclei not coupled to ^{199}Hg . Such an analysis provides information on the ^{31}P CS tensors as well as, for the case of **2**, the ^{31}P - ^{31}P homonuclear spin-spin coupling. There is very little information available in the literature concerning ^{31}P CS tensors in metal-phosphine complexes. In

fact, this study represents only the *second* single-crystal investigation of a ^{31}P CS tensor in a metal-phosphine complex, the other being for Wilkinson's catalyst, $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ (107)!

3.4.1 Phosphorus Chemical Shift Tensors in 1 and 2

The 1:1 Complex. Rotation plots displaying the variation in CS of the two magnetically distinct ^{31}P nuclei of 1 for rotation about each of the three orthogonal NMR cube axes are shown in Figure 3.5 along with the three-parameter least-squares fits. The data has been analyzed in the conventional manner, as outlined in §2.2.2. Note that

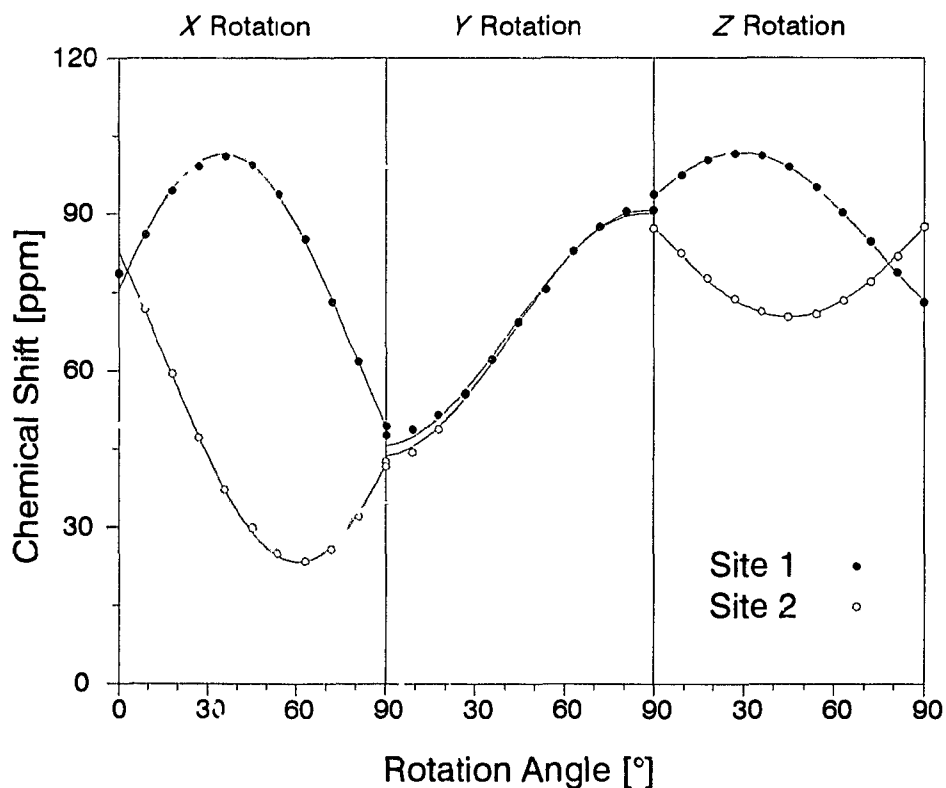


Figure 3.5 NMR single-crystal rotation plots displaying the variation in the ^{31}P CS for the two magnetically distinct sites of 1 for rotations about the three NMR cube axes, as indicated.

small phase angles, ξ , of magnitude -2° and $+3^\circ$ have been applied to the X and Z rotation data, respectively (108). The results of the CS tensor analyses are summarized in Table 3.1. Note that the average of the three principal components of the CS tensor

Table 3.1 Phosphorus Chemical Shift Tensor Data for 1 Obtained From Analysis of the Single-Crystal NMR Data^a

Chemical Shift (ppm) ^{b, c}			Direction Cosines ^d		
Site 1	δ_{11}	110	-0.363	-0.704	-0.606
	δ_{22}	83	-0.422	-0.461	0.784
	δ_{33}	20	-0.831	0.541	-0.134
	$\frac{1}{3}\Sigma\delta_{ii}$	71			
Site 2	δ_{11}	112	-0.397	0.761	-0.518
	δ_{22}	83	-0.412	0.351	0.838
	δ_{33}	23	0.820	0.545	0.170
	$\frac{1}{3}\Sigma\delta_{ii}$	72			

^a The convention used for designating the three principal components of the CS tensor is $\delta_{11} \geq \delta_{22} \geq \delta_{33}$, where δ_{11} and δ_{33} are the least shielded and most shielded principal components, respectively. ^b All chemical shifts are referenced with respect to 85% H_3PO_4 (aq.) at 0 ppm. ^c Errors in the principal components of the ^{31}P CS tensors are estimated to be 1 ppm. ^d The direction cosines are with respect to the orthogonalized crystallographic frame (a^* , b , c).

for each site is in very good agreement with the isotropic chemical shift obtained from a ^{31}P MAS NMR spectrum for a powder sample of 1; $\delta_{\text{iso}} = 72.2$ ppm.

The final step in the CS tensor analysis involved the transformation of each CS tensor PAS into the molecular reference frame. Although there exists a two-fold

ambiguity in assigning the tensors to an individual site within the unit cell, this was resolved by making use of the corresponding orientations of the ^{199}Hg - ^{31}P effective coupling tensors (*vide infra*) as well as local symmetry considerations. As for the former argument, one intuitively anticipates that the unique component of the ^{199}Hg - ^{31}P coupling tensor will be oriented close to the Hg-P bond axis. Examination of both possible assignments of the coupling tensors to the two magnetically distinct sites within the unit cell of **1** reveals that the unique coupling component makes an angle of either 2° or 58° with respect to the Hg-P bond axis. Choosing the former of these two possibilities as the actual assignment results in an orientation of the phosphorus CS tensor depicted in Figure 3.6. Examination of the local site symmetry about the phosphorus atom provides further support for this assignment. As is evident in Figure 3.6, there exists an approximate local mirror plane at the phosphorus atom, bisecting the C(7)-P-C(13) angle. Therefore, one principal component must lie in a direction perpendicular to this plane, while the remaining two components are forced to lie within this plane. Furthermore, the local symmetry of the first coordination sphere about the phosphorus atom contains an approximate C_3 axis, the direction of which corresponds to the Hg-P bond direction. This local symmetry is reflected in the orientation of the CS tensor obtained from the single-crystal ^{31}P NMR study for the assignment depicted in Figure 3.6 only. Note that the component of intermediate shielding is directed normal to the Hg-P-C(1) plane. The most shielded component, δ_{33} , deviates by only 4° from the direction of the Hg-P bond and the approximate C_3 axis.

The 1:2 Complex. The CS tensor rotation patterns obtained for the two

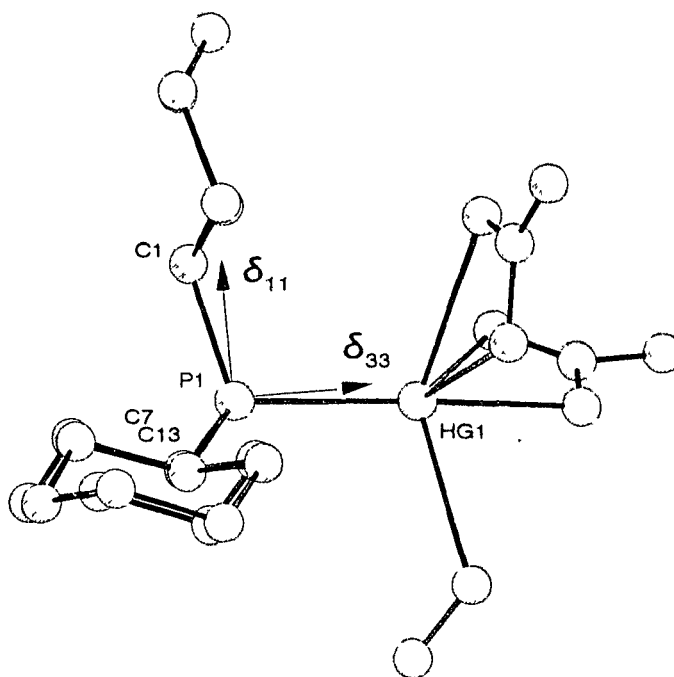


Figure 3.6 The orientation of the principal axis system of the ^{31}P chemical shift tensor in **1** obtained from the single-crystal NMR analysis. The most shielded principal component, δ_{33} , is oriented 4° off the Hg-P bond axis. The intermediate principal component, δ_{22} , was found to lie perpendicular to the plane of projection.

magnetically distinct phosphorus sites of **2** as well as the three-parameter least-squares fits of the data are shown in Figure 3.7. In extracting the two ^{31}P chemical shifts from the single-crystal NMR spectra, an exact analysis (*cf.* Appendix II) was employed in order to account for second-order character observed in the single-crystal ^{31}P NMR spectra. Small phase angles, ξ , of magnitude -5° and $+1^\circ$ have been applied to the X and Z rotation data, respectively. The two ^{31}P CS tensors obtained from this analysis are

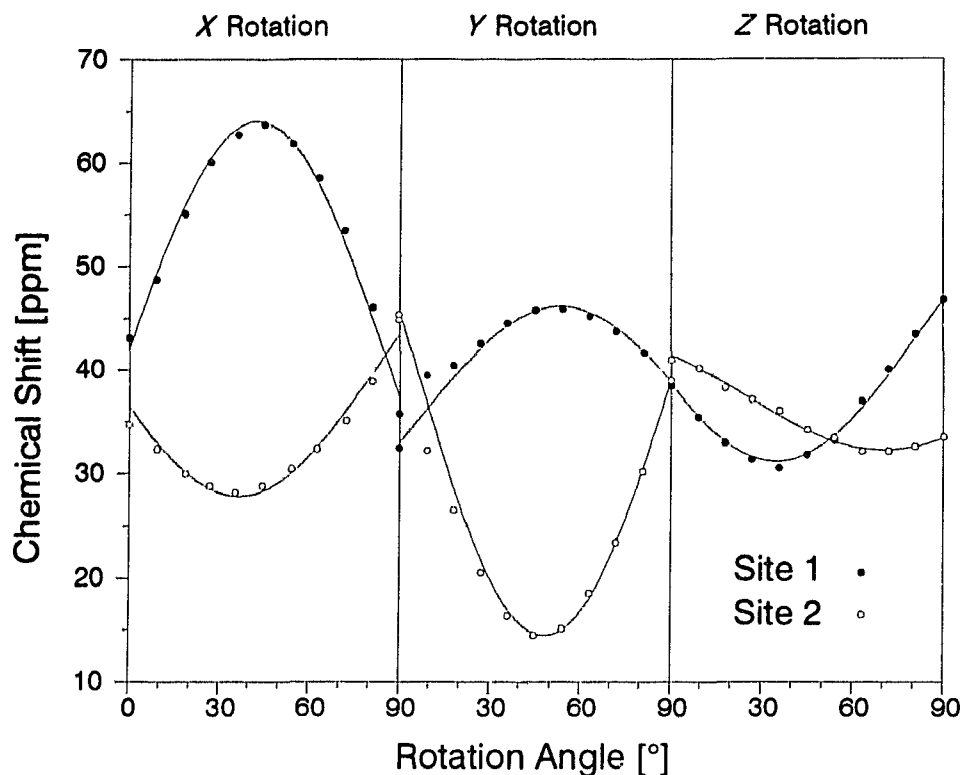


Figure 3.7 NMR single-crystal rotation plots displaying the variation in the ^{31}P CS for the two magnetically distinct sites of **2** for rotations about the three NMR cube axes, as indicated.

summarized in Table 3.2. Note that the calculated isotropic chemical shifts are in very good agreement with that measured from a ^{31}P CP/MAS spectrum of a powder sample of **2**, $\delta_{\text{iso}} = 40.0$ ppm. As well, the magnitudes of the principal components are the same, within experimental error, as those obtained from an analysis of variable-angle-spinning (VAS) spectra of this complex (102).

As was the case for **1**, there exists a two-fold ambiguity in matching the ^{31}P CS tensors to the two magnetically distinct phosphorus sites of **2**, which can be resolved by examining the corresponding orientations of the ^{199}Hg - ^{31}P spin-spin coupling tensors (*vide*

Table 3.2 Phosphorus Chemical Shift Tensor Data for **2** Obtained From Analysis of the Single-Crystal NMR Data^a

Chemical Shift (ppm) ^{b, c}			Direction Cosines ^d		
Site 1	δ_{11}	71	-0.645	-0.721	0.241
	δ_{22}	33	-0.195	0.463	0.865
	δ_{33}	15	-0.738	0.516	-0.440
	$\frac{1}{3}\Sigma\delta_{ii}$	40			
Site 2	δ_{11}	73	0.676	-0.722	-0.163
	δ_{22}	32	0.140	0.343	-0.928
	δ_{33}	14	0.722	0.601	0.333
	$\frac{1}{3}\Sigma\delta_{ii}$	40			

^a The convention used for designating the three principal components of the CS tensor is $\delta_{11} \geq \delta_{22} \geq \delta_{33}$, where δ_{11} and δ_{33} are the least shielded and most shielded principal components, respectively. ^b All chemical shifts are referenced with respect to 85% H_3PO_4 (aq.) at 0 ppm. ^c Errors in the principal components of the ^{31}P CS tensors are estimated to be 2 ppm. ^d The direction cosines are with respect to the orthogonalized monoclinic crystallographic frame (a , b , c^*).

infra). Choosing the solution which yields the largest component of the ^{199}Hg - ^{31}P spin-spin coupling tensors directed approximately along the Hg-P bonds results in orientations of the ^{31}P CS tensors as depicted in Figure 3.8. As for the case of **1**, examination of the local site symmetry about the two phosphorus nuclei provides further support for this assignment. More specifically, the two Hg-P-C(1) planes constitute approximate local mirror planes at the phosphorus nuclei. Only for the assignment depicted in Figure 3.8 is this local symmetry reflected in the orientations of the ^{31}P chemical shift tensors; both δ_{11} and δ_{33} lie within this mirror plane while δ_{22} is directed normal to this plane within

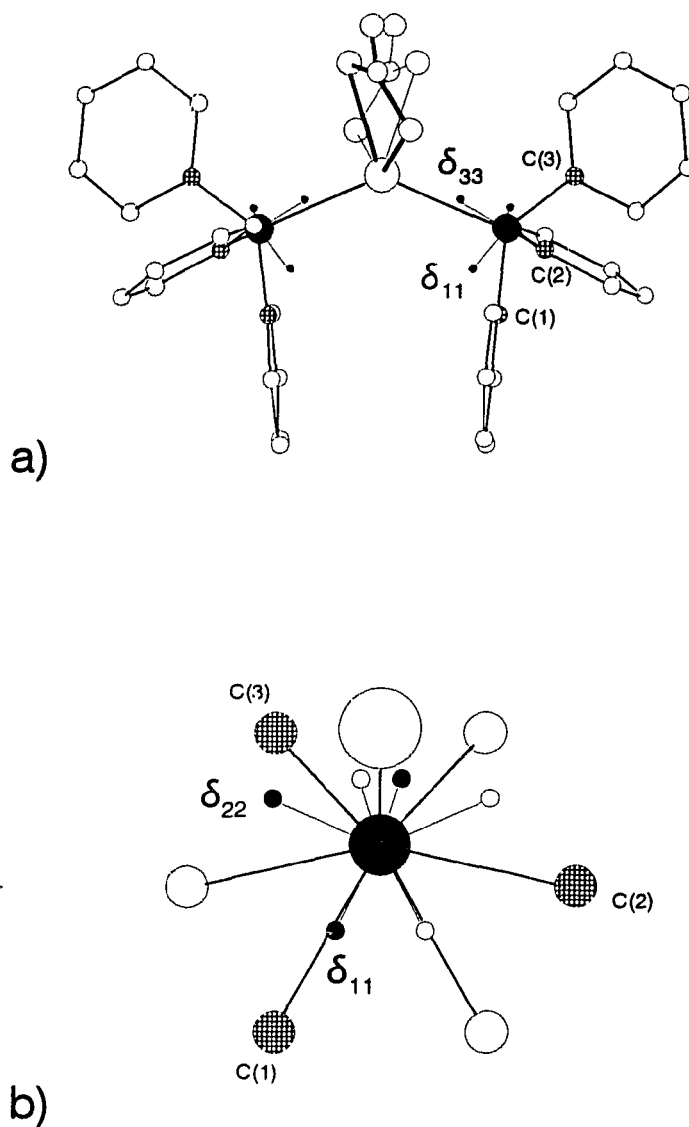


Figure 3.8 Symmetrized orientations of the two ^{31}P CS tensors of **2**. Hydrogen atoms have been omitted for clarity. (a) View such that the P-Hg-P plane is coincident with the plane of the paper. The two magnetically distinct ^{31}P sites are indicated by closed circles while the *ipso* carbon atoms are displayed as crossed circles. Labelling of the CS tensor components and *ipso* carbon atoms has been performed at site 1 only. (b) Projection looking down the P(site 1)-P(site 2) internuclear vector. For this projection, only the *ipso* carbon atoms of the phenyl rings are shown.

experimental error. The angle between the most shielded direction, δ_{33} , and the Hg-P bond axis is 14° . Before producing the CS tensor orientations illustrated in Figure 3.8, the direction cosines in Table 3.2 were symmetrized such that the two ^{31}P CS tensors were constrained to be related by the crystallographic two-fold rotation axis. This exercise enables an estimate of the accuracy of the CS tensor orientations. It was determined that the deviation between eigenvectors in terms of the crystallographic C_2 relationship was 8° for both the intermediately and most shielded components while a deviation of 5° was found for the least shielded component. Considering the uncertainty in the magnitudes of the principal components of the ^{31}P CS tensors as well as the differences between these components, errors of this magnitude are not unexpected (91, 109).

Discussion. As mentioned, the present study represents only the second single-crystal NMR investigation of the ^{31}P CS tensor in a metal-phosphine complex, the other study involving Wilkinson's catalyst (107). Unfortunately, this complex crystallizes in the space group $Pna2_1$ with four magnetically distinct molecules in the unit cell, which presents a fundamental problem as there are, in principle, twelve possible assignments of the phosphorus shielding tensors to orientations in the molecular frame (107). Thus, the lack of well established benchmarks in addressing chemical shift-structure correlations precludes any attempts to rationalize the results obtained here. It is noteworthy that the CS along the mercury-phosphorus bond, 10-35 ppm, observed for **1** and **2** as well as other mercury complexes (82, 83), is rather unusual in comparison with phosphine complexes of other transition metals. Typically, the most shielded direction is associated

with values of -20 to -80 ppm ($M = \text{Mo, W, Mn, Rh, Fe, Ni}$) (107, 110) or 0 to -20 ppm ($M = \text{Pt}$) (84, 111).

The orientations of the ^{31}P CS tensors for both **1** and **2** are qualitatively analogous. The most shielded component lies closest to the Hg-P bond in both species while the least shielded component lies within the plane containing the smallest Hg-P-C bond angle. However, despite the similarities in orientation, the magnitudes of the three principal components show marked differences, with each component more shielded in **2**. Although similar trends in the individual components of the ^{31}P CS tensors have been observed for the free phosphine ligands, PPh_3 and PCy_3 (112), the observed shielding changes in the mercury complexes, relative to the free ligands, are amplified for both the least and intermediately shielded components. The tensor component least affected by the structural changes present within these two complexes is the most shielded component, δ_{33} , oriented closest to the Hg-P bond direction. Although the three Hg-P-C bond angles in **1** are similar (101), with the largest difference approximately 2° , for **2** this is not the case (92f). Specifically, the two Hg-P-C(1) bond angles, $106.2(1)^\circ$, are much smaller than the remaining Hg-P-C angles in the 1:2 complex, with the greatest difference about 10° (92f). The larger departure from three-fold rotation symmetry about the Hg-P bond in **2** may, in part, be responsible for the apparent larger deviation of the most shielded component from the Hg-P bond axis (14°) compared with **1** (4°) as well as the enhanced shielding asymmetry within the plane perpendicular to this component. Finally, the principal components of the ^{31}P CS tensor for the 1:1 species, $[\text{HgPPh}_3(\text{NO}_3)_2]_2$, have been previously determined from NMR studies of a powder

sample of this complex (83). Compared with the analogous 1:2 complex investigated here, both the intermediately and most shielded components have the same magnitudes within experimental error. However, the least shielded component is substantially more shielded in the 1:1 complex ($\delta_{11} = 44$ ppm).

3.4.2 ^{31}P , ^{31}P Spin-Spin Coupling in 2

Since metal-phosphine complexes commonly contain more than one phosphine ligand per molecule, there has been considerable interest in both the magnitude and sign of $^2J(^{31}\text{P}, ^{31}\text{P})_{iso}$ in these species (94, 113). This coupling is known to be sensitive to a variety of structural factors such as the metal involved and its coordination number, the P-M-P bond angle, the electronegativity of the substituents, as well as the stereochemistry of the complex. For example, it is a general observation that $^2J(^{31}\text{P}, ^{31}\text{P})_{trans} > ^2J(^{31}\text{P}, ^{31}\text{P})_{cis}$. Furthermore, the absolute signs of these couplings often differ with the sign for the *trans* geometry positive and the *cis* geometry negative (94). Specifically for the mercury-phosphine complexes, $^2J(^{31}\text{P}, ^{31}\text{P})_{iso}$ generally exhibits a similar dependence on these structural parameters to that of $^1J(^{199}\text{Hg}, ^{31}\text{P})_{iso}$. For example, Allman and Lenkinski have measured $^2J(^{31}\text{P}, ^{31}\text{P})_{iso}$ within a series of 1:2 complexes of the type, $\text{Hg}(\text{PPh}_3)_2(\text{X})_2$, and have found this coupling constant, which ranged from 110 - 240 Hz, to generally increase with the electron withdrawing capability of the anion, X (97). Although $^2J(^{31}\text{P}, ^{31}\text{P})_{iso}$ for 2 was not reported in their study due to the chemical equivalence of the phosphine ligands, this coupling constant has since been measured from slow MAS experiments to be even larger, 250 Hz (102). Similar trends have been

reported for $^1J(^{199}\text{Hg}, ^{31}\text{P})_{\text{iso}}$ in these same 1:2 complexes (92).

The orientation dependence of the splittings observed in the ^{31}P single-crystal NMR spectra due to homonuclear spin-spin coupling between the two phosphorus nuclei has been carefully examined. Given that typical line widths in the single-crystal NMR spectra were on the order of 250 Hz, the relatively small magnitude of this coupling precluded its observation at many orientations of the single crystal, making a reliable least-squares analysis of the coupling data impossible. Nevertheless, the sign of $^2J(^{31}\text{P}, ^{31}\text{P})_{\text{iso}}$ is available from these data. It was observed that the magnitude of the splitting, A (*cf.* Appendix II), reached a maximum when the P-P internuclear vector was oriented perpendicular to the external magnetic field direction. The largest splitting was observed at the $Y(108^\circ)$ orientation, $A = 475$ Hz. These results indicate that the relative sign of the dipolar and J coupling between the two ^{31}P nuclei is the same; thus the absolute sign of $^2J(^{31}\text{P}, ^{31}\text{P})_{\text{iso}}$ is positive. A positive sign has also been reported for $^2J(^{31}\text{P}, ^{31}\text{P})_{\text{iso}}$ in $[\text{Hg}(\text{PMe}_3)_2](\text{NO}_3)_2$ (+250 Hz) (114), the only other determination of both the sign and magnitude of $^2J(^{31}\text{P}, ^{31}\text{P})_{\text{iso}}$ in a mercury-phosphine complex.

3.5 ^{199}Hg - ^{31}P J Tensors in 1 and 2.

The 1:1 Complex. The magnitude of the total observed ^{199}Hg - ^{31}P spin-spin coupling for a given orientation of the single crystal of **1** in the external magnetic field is a function of both the direct and indirect coupling interactions. In analyzing the ^{199}Hg satellite splittings in the single-crystal NMR spectra, $^1J(^{199}\text{Hg}, ^{31}\text{P})_{\text{iso}}$ was first subtracted from the observed splittings, which isolates the magnitude of the coupling due to the

direct dipolar and **anisotropic** indirect spin-spin coupling, exclusively. This parameter has been measured from an MAS spectrum of the same single crystal used throughout this study. The value obtained, 8199 ± 25 Hz, is identical, within experimental error, to that obtained from an MAS spectrum for a powdered sample of **1**.

Rotation patterns showing the variation in the ^{199}Hg - ^{31}P effective dipolar coupling for rotation about the three orthogonal NMR cube axes are illustrated in Figure 3.9. Also displayed are the three-parameter least-squares fits of the data. It should be mentioned that this analysis assumes **J** to be a symmetric tensor; antisymmetry in **J** (32,

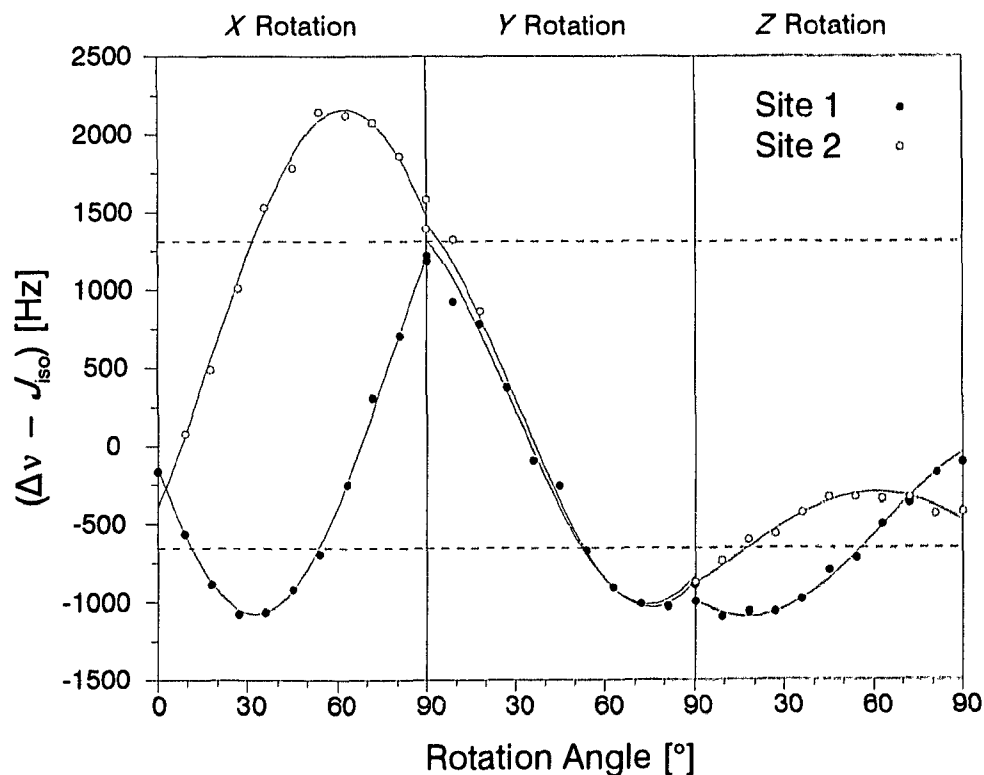


Figure 3.9 NMR single-crystal rotation plots for **1** displaying the variation in the ^{199}Hg - ^{31}P effective dipolar coupling for rotation about the three NMR cube axes, as indicated. The calculated range of the direct dipolar coupling is indicated by dashed lines.

33, 70, 115) has never been experimentally detected and even if non-zero, its influence on the observed spectra would undoubtedly be undetectable (70). The effective dipolar coupling tensors obtained for each of the two magnetically distinct phosphorus sites of **1** are summarized in Table 3.3. As mentioned in §3.4.1, although there exists two

Table 3.3 Effective ^{199}Hg - ^{31}P Dipolar Coupling Tensor Data for **1** Obtained From Analysis of the Single-Crystal NMR Data^a

Effective Coupling (Hz) ^b			Direction Cosines ^c		
Site 1	R_{zz}^{eff}	2368	-0.855	0.481	-0.197
	R_{yy}^{eff}	-1010	-0.494	-0.869	0.031
	R_{xx}^{eff}	-1072	-0.156	0.117	0.980
Site 2	R_{zz}^{eff}	2288	0.842	0.486	0.230
	R_{yy}^{eff}	-1039	0.051	0.359	-0.934
	R_{xx}^{eff}	-1164	0.537	-0.797	-0.271

^a The convention used for designating the three principal components of the effective ^{199}Hg - ^{31}P coupling tensor is $|R_{zz}| \geq |R_{xx}| \geq |R_{yy}|$. ^b Errors in the principal components of the coupling tensors are estimated to be 150 Hz. ^c The direction cosines are with respect to the orthogonalized monoclinic crystallographic frame (a^* , b , c).

possible assignments for the orientation of the effective dipolar coupling tensor in the molecular reference frame, with R_{zz}^{eff} either lying approximately 2° or 58° off the Hg-P bond axis, only the former of these two possibilities is intuitively reasonable. Keeping in mind that these results represent the combination of both the traceless part of the **J** tensor and the ^{199}Hg - ^{31}P dipolar tensor and, furthermore, given the experimental uncertainty associated with R_{xx}^{eff} and R_{yy}^{eff} (cf. Table 3.3), one can therefore immediately

conclude that, within the limits of the present investigation, the ^{199}Hg - ^{31}P **J** tensor in **1** is both axially symmetric and collinear with the dipolar interaction. In other words, the magnitude of the ^{199}Hg satellite splittings, $\Delta\nu$, observed in the ^{31}P single-crystal NMR spectra of **1** can be expressed as:

$$\Delta\nu = J_{iso} - R_{eff}(3\cos^2\theta - 1) \quad (3.1)$$

where R_{eff} is the effective ^{199}Hg - ^{31}P dipolar coupling constant and θ is the angle between the Hg-P bond axis and the external magnetic field. These conclusions will remain implicit throughout the remainder of this discussion.

It is useful to qualitatively examine the rotation plots displayed in Figure 3.9. Of particular interest is the data obtained for rotation about the cube *X* axis. Examination of the projection of the crystal structure of **1** into the cube *YZ* plane reveals that the Hg-P bond vector is oriented at an angle of approximately 9° with respect to this plane. Since the external magnetic field "moves" within the cube *YZ* plane in this rotation plot, it is clear from eq. 3.1 that the range of ^{199}Hg - ^{31}P effective coupling will approximate $3R_{eff}$, which is observed experimentally. This result can be compared with that which would be obtained based exclusively on ^{199}Hg - ^{31}P direct dipolar coupling (*i.e.* $\Delta J = 0$). Such a comparison is depicted in Figure 3.9, where the calculated limits for the direct dipolar coupling (*cf.* eq. 2.13; $R_{DD} = 665$ Hz) are indicated by dashed lines (for ease of comparison, the sign of R_{DD} was taken to be negative). Unquestionably, the experimental findings presented in Figure 3.9 clearly demonstrate that the ^{199}Hg - ^{31}P effective dipolar coupling in **1** possesses a sizeable contribution from an anisotropic ^{199}Hg - ^{31}P **J** tensor.

Furthermore, it is important to emphasize that this result provides irrefutable evidence that the $\mathbf{J}$ tensor is anisotropic; regardless of factors such as motional averaging or the absolute sign of the effective dipolar coupling constant, this conclusion qualitatively remains unaltered.

In order to quantify the contribution from the anisotropic part of the ^{199}Hg - ^{31}P $\mathbf{J}$ tensor to the effective dipolar coupling, knowledge of the absolute sign of the latter term is necessary. Although this information is not directly accessible from the results of the present experiment, the relative signs of $^1J(^{199}\text{Hg}, ^{31}\text{P})_{\text{iso}}$ and R_{eff} can be deduced. The fact that maximum and minimum splittings of approximate magnitude $|^1J_{\text{iso}}| + 2|R_{\text{eff}}|$ and $|^1J_{\text{iso}}| - |R_{\text{eff}}|$, respectively, are experimentally observed (*cf.* Figure 3.9) requires that $^1J_{\text{iso}}$ and R_{eff} be of opposite sign. Consequently, since $^1J(^{199}\text{Hg}, ^{31}\text{P})_{\text{iso}}$ has previously been found to be positive (93, 116, 117), the absolute sign of the effective ^{199}Hg - ^{31}P dipolar coupling is concluded to be negative. With this information, the contribution from the known ^{199}Hg - ^{31}P direct dipolar coupling can be separated from the effective coupling tensor to isolate the traceless component of the ^{199}Hg - ^{31}P $\mathbf{J}$ tensor. The results of this analysis are summarized in Table 3.4.

In an effort to perform an independent verification of the single-crystal NMR results, ^{31}P NMR spectra for a static powder sample of **1** have been obtained at applied field strengths of 4.7 T and 9.4 T. The spectrum obtained at 4.7 T is presented in Figure 3.10. Also illustrated in this same figure is the calculated line shape obtained using the parameters extracted from analysis of the single-crystal NMR data. The agreement between the experimental and calculated line shapes at both applied fields is

Table 3.4 The Three Principal Components of the Traceless Part of the ^{199}Hg - ^{31}P J Tensor (in Hz) for **1**^a

	site 1	site 2
$J_{zz} - J_{iso}$	3698	3618
$J_{yy} - J_{iso}$	-1675	-1704
$J_{xx} - J_{iso}$	-1737	-1829
ΔJ	5404	5385

^a Obtained from the effective dipolar coupling tensor (*cf.* Table 3.3) by subtracting out the direct dipolar coupling contribution. The convention used for designating the three principal components of the ^{199}Hg - ^{31}P J tensor is $|J_{zz} - J_{iso}| \geq |J_{xx} - J_{iso}| \geq |J_{yy} - J_{iso}|$. Errors in the above numbers are estimated to be 150 Hz.

very satisfactory, in support of the single-crystal NMR results. It is apparent from the experimental spectrum in Figure 3.10 that analysis of such a powder pattern is indeed a non-trivial task. This analysis is further compounded in **1** due to the fact that the ^{199}Hg satellite powder patterns are partially embedded within the central line shape which, as mentioned earlier, arises from anisotropic ^{31}P chemical shielding. Although such a system is amenable to analysis using slow-spinning MAS experiments, clearly the single-crystal NMR experiment is a more general and reliable approach.

The 1:2 Complex. A full three-dimensional analysis of the ^{199}Hg - ^{31}P spin-spin coupling tensors in **2** has not been performed due to difficulties in reliably analyzing the satellite peaks obtained for rotation about the cube Z axis. Within the first 60° of this rotation pattern, the maximum chemical shift difference between the two ^{31}P nuclei is only on the order of 4 ppm. Furthermore, the ^{31}P - ^{31}P dipolar vector is oriented just 14° off the rotation axis, resulting in relatively large ^{31}P - ^{31}P spin-spin interactions which

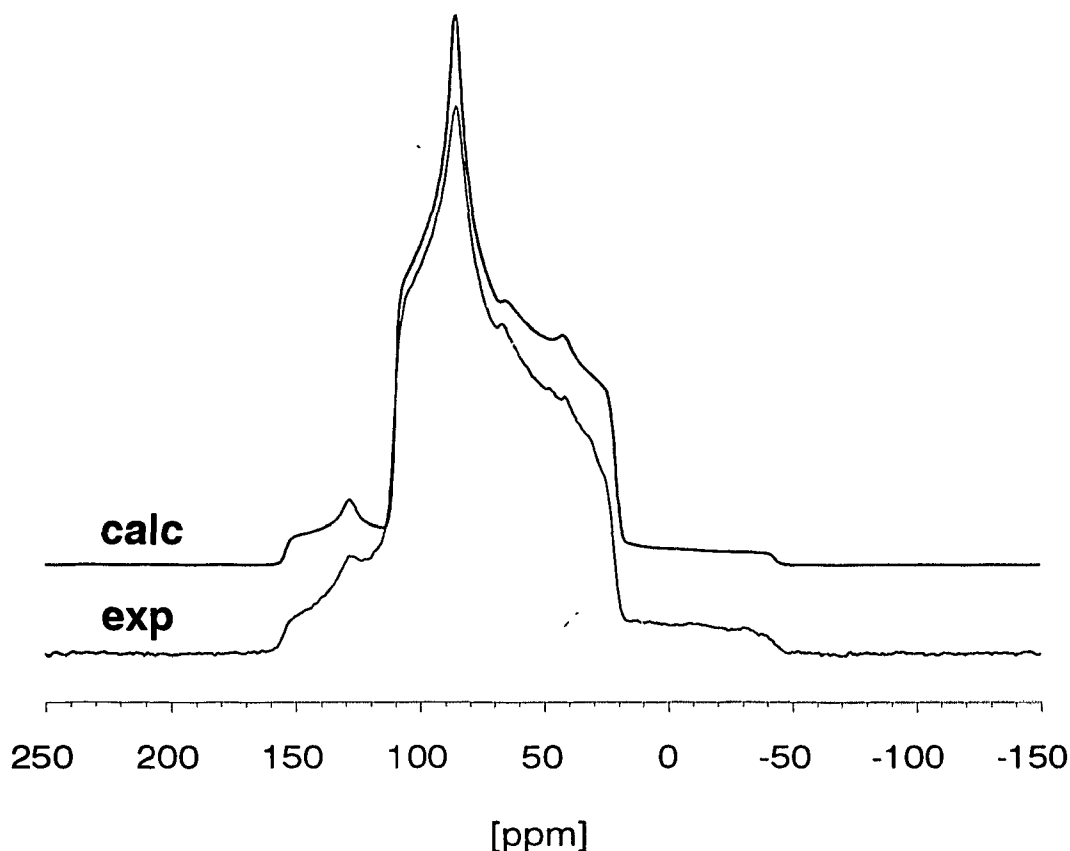


Figure 3.10 The experimental (bottom) and calculated (top) ^{31}P NMR spectrum for a static powder sample of **1** at an applied field strength of 4.7 T. The calculated spectrum was obtained using the following parameters, obtained from the single-crystal NMR analysis; $\delta_{11} = 110$ ppm, $\delta_{22} = 84$ ppm, $\delta_{33} = 21$ ppm, $J_{\text{iso}} = +8199$ Hz, $R_{\text{eff}} = -1135$ Hz, $\alpha = 0^\circ$, and $\beta = 4^\circ$.

varied little with orientation throughout this rotation pattern. Consequently, some of the most tightly-coupled second-order spectra observed in this study were obtained within the first 60° of the Z rotation pattern. The ^{199}Hg satellite peaks exhibited relatively little orientation dependence and appeared as featureless, broad humps. With similar spectral features evident near the end of this rotation pattern, a conventional least-squares analysis of the ^{199}Hg - ^{31}P spin-spin coupling data was not possible.

Despite these difficulties, reliable information concerning the anisotropy in the ^{199}Hg - ^{31}P $\mathbf{J}$ tensors can be deduced from the X and Y rotation patterns. It was observed that when the ^{199}Hg - ^{31}P internuclear vectors were oriented approximately along the external magnetic field direction, maxima were observed in the corresponding ^{199}Hg satellite splittings. Given the well-known orientation dependence of the dipolar interaction relative to the molecular reference frame, this finding indicates that the largest component of the ^{199}Hg - ^{31}P $\mathbf{J}$ tensor is oriented along the Hg-P bond direction within experimental error. Furthermore, considering the results obtained for **1**, it is reasonable to assume that the $\mathbf{J}$ tensor is axially symmetric so that the splittings between the ^{199}Hg sub-spectra, $\Delta\nu$, can be expressed as in eq. 3.1.

Displayed in Figure 3.11 is the observed orientation dependence of the ^{199}Hg satellite splittings obtained for rotation about the cube X axis. Note that the isotropic J coupling constant, $^1J(^{199}\text{Hg}, ^{31}\text{P})_{\text{iso}} = 5550$ Hz, obtained from an independent CP/MAS experiment, has been subtracted from the measured splittings, thereby isolating coupling contributions due to dipolar and **anisotropic** J coupling only. As well, the horizontal dashed line in this figure indicates the theoretical maximum value of the effective ^{199}Hg - ^{31}P dipolar coupling due to direct dipolar coupling alone (*i.e.* in the absence of an anisotropic $\mathbf{J}$ tensor), $2R_{\text{Hg-P}} = 1200$ Hz. Note that this result has been derived using a Hg-P bond length of 2.451 Å obtained in the X-ray diffraction study of Buergi *et al.* (92f). The fact that the observed splittings exceed this maximum for site 1 at many orientations immediately indicates that the ^{199}Hg - ^{31}P $\mathbf{J}$ tensor in **2** is anisotropic. Based upon the observed extrema in the X and Y rotation patterns, a value for R_{eff} can be

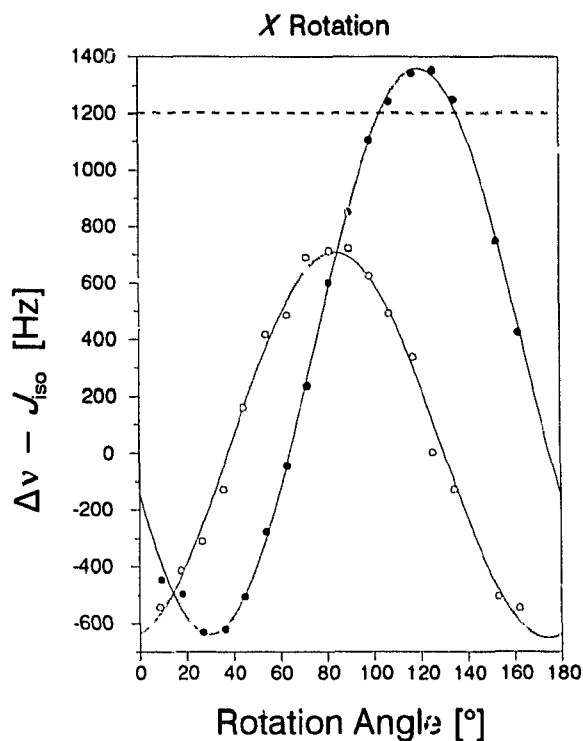


Figure 3.11 Variation in the ^{199}Hg - ^{31}P effective dipolar coupling obtained for rotation about the cube X axis (site 1: $\bullet$ site 2: $\circ$). The horizontal dashed line indicates the maximum coupling in the absence of an anisotropic ^{199}Hg - ^{31}P $\mathbf{J}$ tensor.

calculated from eq. 3.1 provided that the orientation of the corresponding Hg-P internuclear vector is known relative to the cube plane within which the external magnetic field probes. For the rotation patterns displayed in Figure 3.11, the two Hg-P vectors are calculated to project 7° and 30° out of the cube YZ plane for sites 1 and 2, respectively. Examination of the X and Y coupling data in this fashion yields the result, $R_{\text{eff}} = 725 \pm 150$ Hz. Furthermore, the fact that maximum satellite splittings for a particular site were observed when the external magnetic field was oriented approximately parallel with the corresponding Hg-P internuclear vector indicates that the

absolute sign of R_{eff} is opposite to that of J_{iso} . Given that the sign of $^1J(^{199}\text{Hg}, ^{31}\text{P})_{iso}$ has previously always been found to be positive (93, 116, 117), the absolute sign of R_{eff} must be negative. Consequently, this result enables calculation of the anisotropy in the ^{199}Hg - ^{31}P $\mathbf{J}$ tensor, $\Delta J = 4.0 \pm 0.5$ kHz.

In order to provide independent support of the single-crystal NMR data, ^{31}P NMR spectra for a static powder sample of **2** have been obtained at two different applied magnetic fields. A computer program has been written (*cf.* Appendix II) in order to calculate these spectra using the parameters derived from the single-crystal analysis. The results for the experimental and calculated ^{31}P spectra at both 4.7 and 9.4 T are shown in Figure 3.12. The agreement between the experimental and calculated spectra is very good, in support of the single-crystal NMR data. Clearly, these powder spectra are very complicated and, in the absence of single-crystal data, would be impossible to analyze.

Discussion. It is instructive to examine qualitatively the implications of an anisotropic J coupling. For this purpose, consider a hypothetical ^{31}P NMR spectrum for a powder sample of **1** in the absence of both phosphorus chemical shielding and ^{199}Hg - ^{31}P direct dipolar coupling. In Figure 3.13, the ^{199}Hg - ^{31}P $\mathbf{J}$ tensor has been illustrated in the conventional ellipsoidal representation. When the magnetic field lies parallel to the Hg-P bond, the J coupled nuclei are polarized parallel to the Hg-P bond axis, yielding a J coupling of $J_{\parallel} = 11.8$ kHz (see Figure 3.13). However, when the external field lies perpendicular to this axis, the spins are aligned in a direction perpendicular to the Hg-P bond axis. Under these conditions, the observed J coupling is $J_{\perp} = 6.4$ kHz. Finally, it is clear that when the spins are polarized at the magic angle with respect to the Hg-P

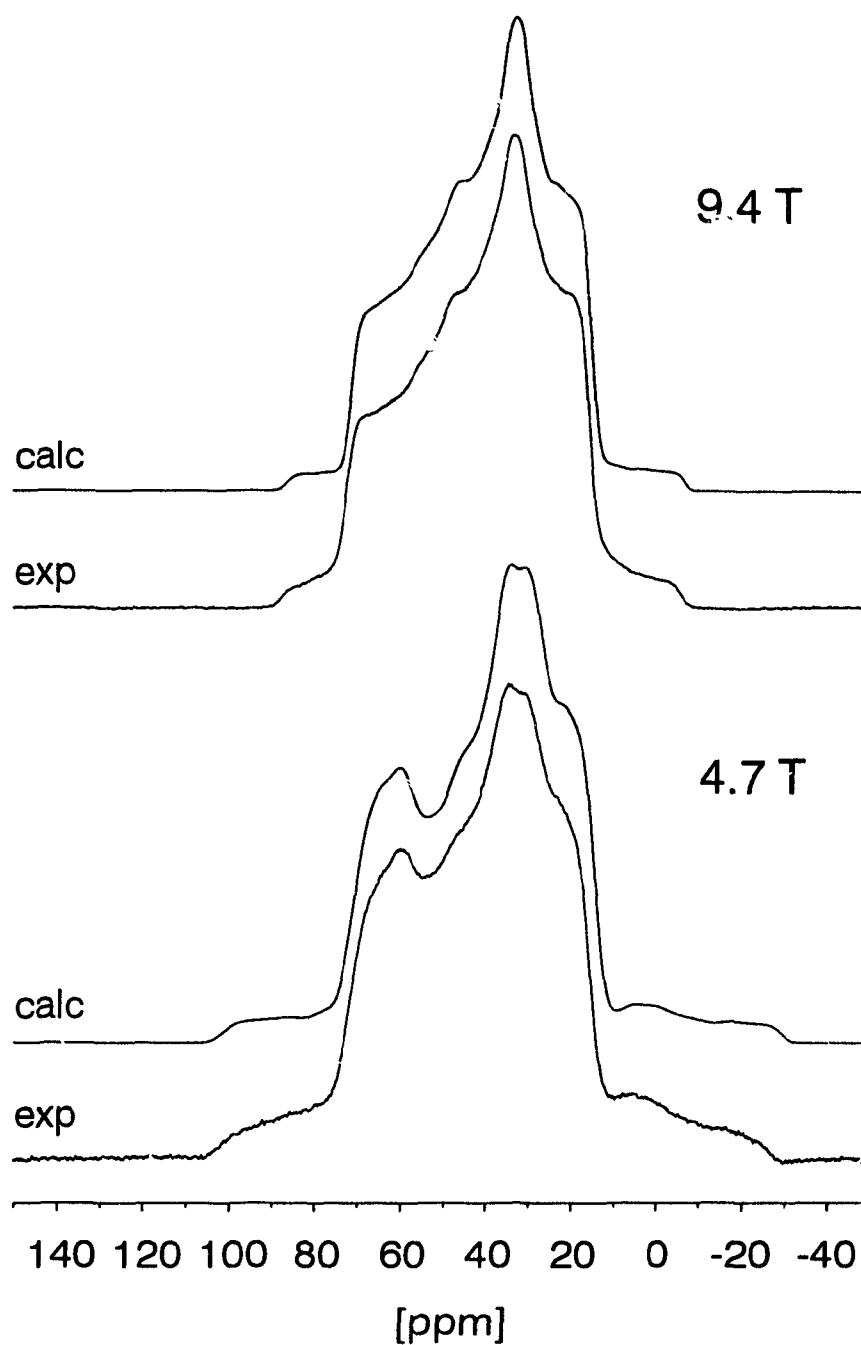


Figure 3.12 Experimental and calculated ^{31}P NMR spectra obtained for a static powder sample of **2** at two different applied magnetic fields. The calculated spectra have been generated using the data obtained from the single-crystal NMR study. Note that the calculated spectra have been convoluted with a Gaussian line broadening function of magnitude 500 Hz (9.4 T) and 350 Hz (4.7 T).

bond axis, the isotropic J coupling, $J_{iso} = 8.2$ kHz, is observed. Considering all possible orientations of the Hg-P bond axis over the surface of the ellipse in this fashion yields the powder spectrum depicted in Figure 3.13.

The ^{31}P single-crystal NMR results for **1** and **2** reveal an anisotropy in the ^{199}Hg - ^{31}P $\mathbf{J}$ tensor which is comparable to the isotropic coupling constant, on the order of 70% in both species. The fundamental conclusion to be derived from this result is that mechanisms other than FC are operative and make substantial contributions to the transmission of nuclear spin information between ^{199}Hg and ^{31}P nuclei in these systems. These findings contribute to a growing body of evidence that mercury-phosphorus indirect spin-spin couplings are anisotropic in nature (80, 82, 83). Furthermore, there is also an increasing amount of evidence that transition metal-phosphorus J couplings are, in general, anisotropic (84, 86, 118). Although the status of the current understanding of indirect spin-spin couplings prohibits resolution of these anisotropic couplings in terms of the contributing mechanisms, it is clear that interpretation of metal-phosphorus isotropic coupling constants using concepts based on the FC mechanism alone is an oversimplified approach. Although trends in these data may apparently be rationalized using such simplistic ideas, extreme caution must be exercised without knowledge of the behaviour of the non-contact mechanisms. Although reliable theoretical calculations of $\mathbf{J}$ tensors in such systems would be invaluable to our understanding of these data, it is unfortunate that such systems impose formidable barriers to a successful theoretical treatment. Nevertheless, it is anticipated that reliable experimental measurements of $\mathbf{J}$ tensors, as in this investigation, will compel theoreticians to intensify their efforts in

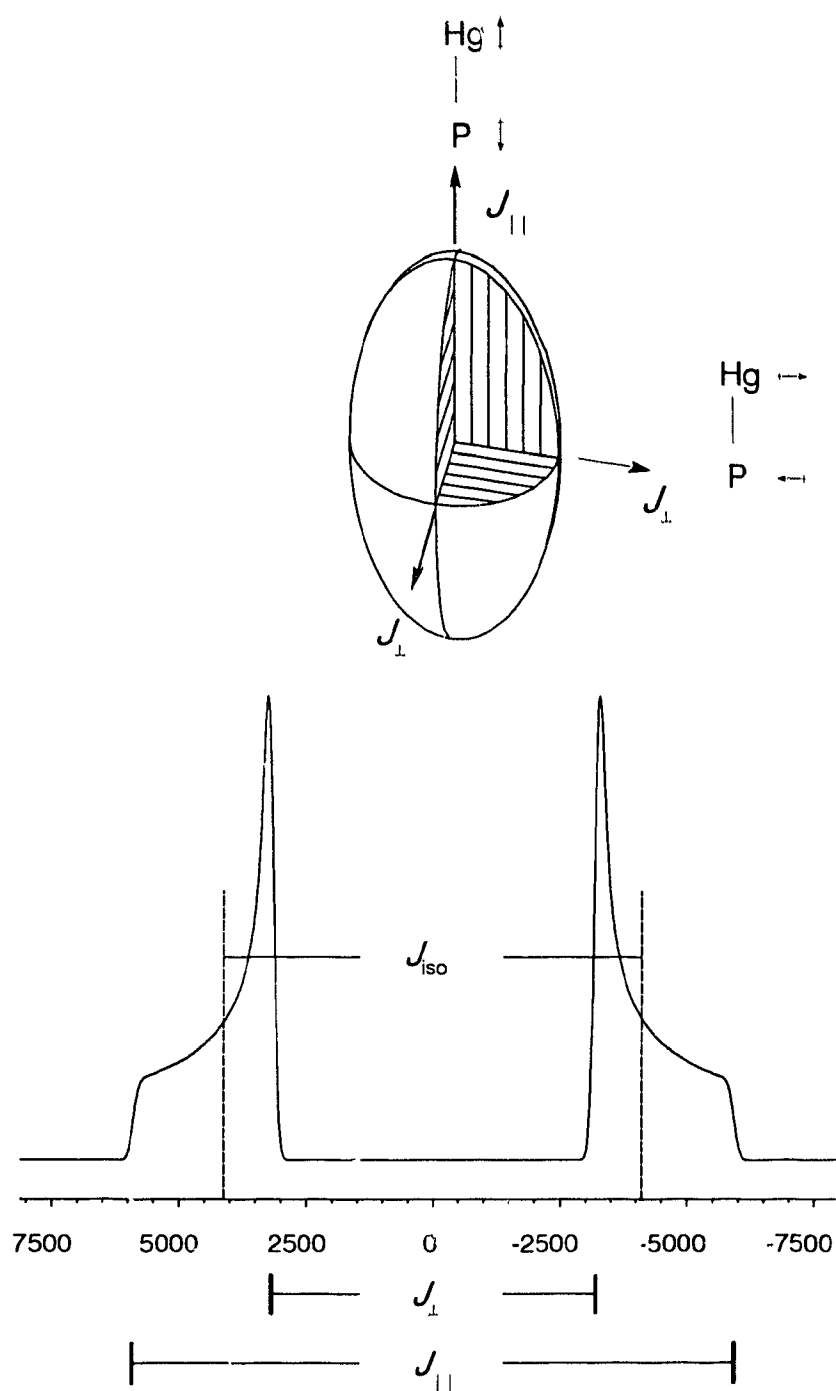


Figure 3.13 A hypothetical ^{31}P NMR powder spectrum for **1**, obtained by considering the ^{199}Hg - ^{31}P J interaction only. The anisotropy in the J tensor was taken to be 5.4 kHz. The magnitudes of the indicated couplings are as follows: $J_{\parallel} = 11.8$ kHz, $J_{\perp} = 6.4$ kHz, and $J_{\text{iso}} = 8.2$ kHz.

advancing the current level of theory concerning the calculation of indirect spin-spin coupling tensors. Further single-crystal NMR measurements of **J** tensors are presently underway in our laboratory.

3.6 Conclusions

In this chapter, ^{31}P single-crystal NMR spectroscopy has been employed to study both a 1:1 and 1:2 mercury-phosphine complex. For the first time, unequivocal experimental data has been obtained for the orientation of a ^{31}P CS tensor in a metal-phosphine complex. As well, the sign of $^2J(^{31}\text{P}, ^{31}\text{P})_{\text{iso}}$ in a 1:2 mercury-phosphine complex has been measured and been found to be positive. The most exciting results of this work involve the accurate measurement of large anisotropic ^{199}Hg - ^{31}P **J** tensors in both of these species. Such findings are significant as they indicate the importance of non-Fermi contact mechanisms in mediating the ^{199}Hg - ^{31}P indirect spin-spin coupling. These results are a reminder of the fact that interpretation of metal-phosphorus **J** couplings based on concepts that ignore mechanisms other than FC is an oversimplified approach. As well, these findings illustrate the importance of looking at the **J** tensor rather than merely the isotropic value. Finally, for both compounds investigated here, the single-crystal data has been verified by performing calculations of the NMR spectrum for powder samples and comparing with the experimental spectra. Such procedures are standard in this laboratory and should be an essential ingredient of any single-crystal NMR experiment.

Chapter 4

A Comparative Investigation of the Carbon Chemical Shift Tensors in the Carbonyl and Thiocarbonyl Fragments. The Interplay of Experiment and Theory.

4.1 Introduction

A vast amount of experimental data exists for the three principal components of the carbonyl carbon CS tensor in a variety of organic and organometallic carbonyls (119). In particular, the carbonyl carbon CS tensor has found widespread application in structural studies of small peptides and proteins, being sensitive to structural features such as peptide backbone conformation, secondary structure, and hydrogen bonding (120). The carbonyl carbon CS tensor has also been heavily exploited in the characterization of polypeptide structure and dynamics in lipid bilayers (121). There has also been a recent surge in the application of *ab initio* carbon chemical shielding tensor calculations to the study of polypeptide structure, using both Hartree-Fock level theory (122) as well as, more recently, density functional theory (123). In light of this sensitivity of the carbonyl carbon chemical shielding interaction to polypeptide structure and dynamics, a thorough understanding of the carbon CS tensor within the basic amide fragment is compulsory. To this end, several reports have appeared in the literature with emphasis on the characterization of the amide carbon CS tensor using a variety of solid-state NMR techniques (119, 121d, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133).

Despite the large amount of data available for the principal components of the

carbonyl carbon CS tensor in amides and other carbonyl-containing compounds, much less is available for the orientation of these components in the molecular reference frame. For example, the complete carbon CS tensor has been investigated for only one simple organic amide, that for a single crystal of acrylamide (125). This is somewhat surprising considering the natural availability of the ^{13}C - $^{14,15}\text{N}$ spin pair which can be used to characterize the orientation of the carbon CS tensor using the dipolar-chemical shift NMR method (*cf.* §2.2.1). A survey of the available orientation data for the C=O group indicates that the most shielded component, δ_{33} , invariably lies normal to the X-C(O)-Y plane while the intermediately shielded component, δ_{22} , lies within this plane and closest to the C=O bond axis. Although this orientation appears to be general for the carbonyl fragment (134, 135), local variations do exist, particularly for the two in-plane components, which can be exploited to gain information concerning local molecular structure and symmetry.

It is also informative to compare the carbon chemical shielding in the C=O group with that in the thiocarbonyl fragment, C=S. Typically, such studies have been performed using solution NMR and have revealed the isotropic CS in the thiocarbonyl group to be more deshielded than for an analogous carbonyl-containing molecule (136). This phenomenon has generally been interpreted to be the result of a decreased $n \rightarrow \pi^*$ energy gap in the thiocarbonyls, resulting in an enhanced deshielding due to the paramagnetic shielding term (137). However, in the absence of knowledge concerning the CS *tensors* in these species, such arguments are without justification. Unfortunately, very little information is available for thiocarbonyl carbon CS tensors. In fact, it appears

that only five reports involving the measurement of thiocarbonyl carbon CS tensors exist in the literature (*138, 139, 140, 141, 142*). None of these studies involved measurement of the orientation of the CS tensor, information essential in order to elucidate the origin(s) of the thiocarbonyl carbon deshielding observed in solution NMR. Only one of these investigations involved an organic thiocarbonyl compound (*139*). In that study, the thiocarbonyl carbon CS tensor of thiobenzophenone was compared with the carbonyl carbon CS tensor in benzophenone using solid-state ^{13}C NMR spectroscopy of powdered samples. Although large differences in the magnitudes of the three principal components were observed, orientation information was not available from these powder studies. In an earlier ^{13}C single-crystal NMR investigation of benzophenone (*143*), it was concluded that the least shielded component lies perpendicular to the carbonyl bond and in the C-C(O)-C plane while the component of intermediate shielding is oriented along the carbonyl bond. Consequently, based on the observed differences in the magnitudes of the three principal components of the carbon CS tensors as well as simple electronic structure arguments, it was proposed that the two in-plane principal components exchange orientation in thiobenzophenone relative to benzophenone. The most shielded direction was predicted to lie perpendicular to the C-C(S)-C plane.

The research in this chapter involves an effort to characterize and thus compare the complete C=O and C=S carbon CS tensors within a series of small organic amides and thioamides. Experimental carbon CS tensors have been measured using the dipolar-chemical shift NMR technique by focusing on the ^{13}C - ^{14}N as well as the ^{13}C - ^{15}N spin pairs in isotopically enriched powder samples of these compounds. Such studies of

simple amides are important as they serve as models to improve our understanding of the carbonyl carbon chemical shielding within the peptide linkage of larger biological molecules such as proteins. The results for the thioamides represent the first determinations of the orientation of the carbon CS tensor within the C=S group. This information provides, for the first time, concrete evidence as to the origins of the well-known deshielding observed for thiocarbonyls relative to carbonyls. Also, these results permit an assessment of the proposals put forth by Kempf *et al.* concerning the benzophenone/thiobenzophenone system (139). The focus of this chapter is not simply to catalogue CS tensor data for the C=O and C=S groups but rather to try and interpret these data using concepts familiar to chemists. In this respect, *ab initio* chemical shielding tensor calculations have been a tremendous tool for providing insight into the experimental NMR data. As well, the calculations help to alleviate ambiguities inherent in the dipolar-chemical shift NMR technique and therefore have been used extensively throughout this study. Finally, at a much broader level, this work is illustrative of the importance of examining both the principal components and orientation of CS tensors when employing chemical shifts to study molecular structure.

The remainder of this chapter has been organized in the following manner. In §4.2, experimental details will be provided. Although several different amide/thioamide combinations have been investigated, in §4.3 the ^{13}C NMR spectra and analysis will be presented for one pair only, in order to avoid redundancy. Namely, the spectra obtained for 4'-methoxyacetanilide and 4'-methoxythioacetanilide and their analysis are provided as an illustrative example. In §4.4, both the experimental and theoretical results will be

presented and discussed. Finally, §4.5 will contain some concluding remarks.

4.2 Experimental Section

Amide Preparations. Acetanilide- ^{15}N , $^{13}\text{C}(\text{CO})$ was prepared by adding a solution containing 1.00 g (12.6 mmol) of acetyl chloride- $^{13}\text{C}(\text{CO})$ (99%) in 10 mL of chloroform to a mixture of 1.19 g (12.6 mmol) of aniline- ^{15}N (99%) and 4.00 g of sodium carbonate in 25 mL of chloroform (144). The addition was performed over a period of 15 min such that the temperature was maintained below 50 °C. The solution was stirred for 1 h and, after filtration, concentrated on a rotary evaporator to yield white crystals of acetanilide- ^{15}N , $^{13}\text{C}(\text{CO})$. 4'-methoxyacetanilide- $^{13}\text{C}(\text{CO})$ was also prepared in this manner with *p*-anisidine as a starting reagent.

N-methylacetanilide- ^{15}N , $^{13}\text{C}(\text{CO})$ was prepared *via* the acetylation of *N*-methylaniline, which was first synthesized according to a standard literature procedure (145). The acetylation was carried out by refluxing for 1 h a mixture of 1.07 g (9.9 mmol) of *N*-methylaniline- ^{15}N with an excess of acetic anhydride- $^{13}\text{C}_2(\text{CO})$ (99%). The mixture was then poured over crushed ice and neutralized with 5% NaOH (aq) to precipitate white crystals of *N*-methylacetanilide- ^{15}N , $^{13}\text{C}(\text{CO})$.

Acetamide- $^{13}\text{C}(\text{CO})$ (10%) was prepared by adding a mixture of 250 mg (3 mmol) of acetyl chloride- $^{13}\text{C}(\text{CO})$ and 2.25 g (29 mmol) of acetyl chloride to 10 g (86 mmol) of concentrated aqueous ammonia at -4 °C (146). The solvent was then allowed to evaporate and the acetamide was separated from the ammonium chloride by dissolving in hot ethyl acetate and filtering. The 10% labelled acetamide- $^{13}\text{C}(\text{CO})$ was collected by

filtration after the ethyl acetate had cooled to room temperature.

Thioamide Preparations. The thioamides used in this study were obtained by converting the corresponding amides using Lawesson's reagent (LR) (147). 10% labelled thioacetamide- $^{13}\text{C}(\text{CS})$ was prepared by addition of 1.1 g (2.7 mmol) of LR to 0.32 g (5.4 mmol) of 10% labelled acetamide- $^{13}\text{C}(\text{CO})$ in THF which was pre-dried over calcium hydride. The solvent was allowed to evaporate under a stream of nitrogen gas and the resulting mixture was separated on a silica gel column (12:1 dichloromethane: diethylether). Note that thioacetamide appeared to decompose under reduced pressure. The remaining thioamides were prepared analogously except that the solvent was evaporated under vacuum.

Solid-State NMR. All ^{13}C solid-state NMR spectra were acquired at 50.3 MHz on a Bruker MSL-200 spectrometer ($B_0 = 4.7\text{ T}$) and at 100.6 MHz on a Bruker AMX-400 spectrometer ($B_0 = 9.4\text{ T}$). For the MSL, samples were packed into 7 mm (outer diameter) zirconium oxide rotors. For the AMX, 4 mm zirconium oxide rotors were used. Cross polarization (CP) under the Hartmann-Hahn matching condition was used to increase the sensitivity of all the spectra acquired in this study with typical contact times between 5 and 6 ms. High-power ^1H decoupling was used during the acquisition of all spectra. The recycle delay time used for 4'-methoxyacetanilide- $^{13}\text{C}(\text{CO})$ and 4'-methoxythioacetanilide- $^{13}\text{C}(\text{CS})$ was 10 s. For the remaining compounds, long proton spin-lattice relaxation times dictated the usage of the FLIPBACK pulse sequence (98) with typical recycle delay times of 30-60 s. Carbon chemical shifts were referenced to tetramethylsilane (TMS) by setting the high-frequency carbon signal of adamantane to

38.56 ppm (CH₂).

NMR Line Shape Calculations. Calculations of ¹³C NMR powder pattern line shapes were performed on a 486 personal computer using the program *SOLIDS* (44) which incorporates the POWDER routine (99). The approach employed here for analyzing the ¹³C solid-state NMR spectra has been to first use the dipolar-splitting-ratio technique (44) to obtain initial guesses for the polar angles α and β . Consequently, this set of solutions was reduced by considering reasonable values for the carbonyl carbon-nitrogen dipolar coupling in amides and thioamides in conjunction with local symmetry considerations. The corresponding values for α , β , and R_{eff} were then optimized by maximizing the agreement between the experimental and calculated dipolar-chemical shift NMR spectra. In order to emphasize this agreement in the regions of the shoulders and discontinuities of the powder patterns, these comparisons were performed by examining both the first and second derivatives of the static powder pattern line shapes (130).

Carbon Chemical Shielding Tensor Calculations. Calculations of the carbonyl or thiocarbonyl carbon chemical shielding tensors of formaldehyde, thioformaldehyde, formamide, thioformamide, acetamide monomer and dimer, and thioacetamide were carried out on an IBM RS6000/580 workstation using a direct version of the TEXAS 90 *ab initio* program package (148) which implements the GIAO method (54). A Dunning TZP basis set augmented with two sets of polarization functions on all atoms was employed. The geometries of formamide and thioformamide were optimized using GAUSSIAN 92 (149) and a 6-311G(d,p) basis set. Experimental geometries were used for the remaining molecules (150, 151, 152). The carbonyl or thiocarbonyl carbon

chemical shielding tensors of acetamide and thioacetamide have also been calculated on a Silicon Graphics Indigo² XL workstation using the LORG method (56, 153) and a 6-311+G(3d,2p) basis set. The prerequisite SCF wave functions for the LORG calculations were generated using GAUSSIAN 92 (149). Calculations of the carbonyl carbon shielding tensors of the acetanilides were performed on Convex C210 and IBM RS6000/560 workstations using a direct version of the IGLO method (154). The atomic orbital (AO) basis set used was the standard basis II (55) which can be represented as [51111,2111,1] for first-row atoms (*d* exponent 1.0 for C, N, and O) and [311,1] for hydrogen (*p* exponent 0.7). With this basis set, a total of 274 and 308 basis functions were used in the acetanilide and *N*-methoxyacetanilide calculations, respectively! The geometries of the acetanilides were obtained from the X-ray crystal structures (155, 156).

4.3 Carbon-13 Powder Pattern Analyses

4'-methoxyacetanilide. The experimental ¹³C NMR spectra obtained for a static powder sample of 4'-methoxyacetanilide-¹³C(CO) (1) at external magnetic field strengths of 4.7 T and 9.4 T are presented in Figure 4.1. Also shown are the calculated spectra which have been found to best fit the experimental data. By using two different magnetic field strengths, the three principal components of the carbon CS tensor can readily be obtained by finding the spectral singularities which are invariant to the external field strength (in ppm units). The calculated spectra were obtained using the following parameters: $\delta_{11}=246 \pm 2$ ppm, $\delta_{22}=177 \pm 2$ ppm, $\delta_{33}=92 \pm 2$ ppm, $\alpha=29 \pm 3^\circ$, $\beta=90 \pm 2^\circ$, $R_{\text{eff}}=895 \pm 40$ Hz. The spectral simulations are in very good agreement

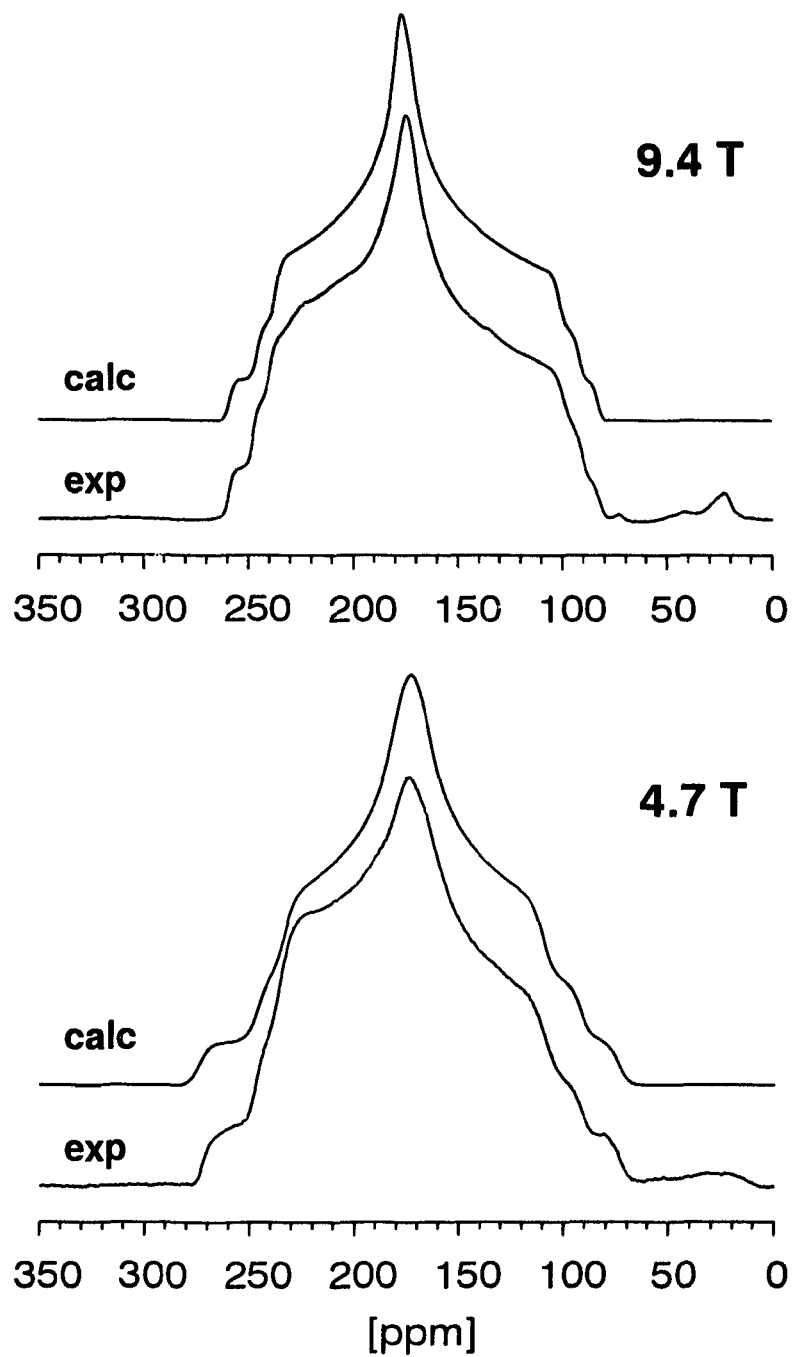


Figure 4.1 Experimental and calculated ^{13}C NMR spectra for a static powder sample of 1 at external magnetic field strengths of 4.7 T and 9.4 T, as indicated.

with the experimental spectra at both external magnetic field strengths employed in this study. Note that the spectra obtained at the two magnetic field strengths exhibit significant differences from one another. In particular, a large asymmetry is observed in the dipolar splittings for the δ_{11} region of the spectrum at 4.7 T. At 9.4 T, this asymmetry is significantly attenuated and is qualitatively due to the increased magnitude of the carbon CS tensor with respect to the ^{13}C - ^{14}N dipolar interaction at the larger external field strength (44, 133). Finally, given the fact that the dipolar interaction is axially symmetric about the dipolar vector axis and considering the local mirror plane defined by the O=C-N fragment, the result that $\alpha=29^\circ$ and $\beta=90^\circ$ is consistent with two possible orientations of the CS tensor PAS in the molecular reference frame (*cf.* Figure 4.2). Assuming the molecular geometry within the amide plane of **1** to be analogous to that in acetanilide (155), these correspond to orientations of the PAS such that (a) the two in-plane components, δ_{11} and δ_{22} , lie approximately perpendicular and parallel to the C=O bond axis, respectively, or (b) these components lie at angles of approximately 30° and 60° , respectively, with respect to this axis. As mentioned, it is well-established that the former of these two orientations is invariably observed for the carbonyl fragment (134, 135). Also, it is the former orientation that is consistent with the *ab initio* MO calculations (*vide infra*).

4'-methoxythioacetanilide. In Figure 4.3, ^{13}C NMR spectra obtained at 9.4 T for static powder samples of 4'-methoxythioacetanilide- $^{13}\text{C}(\text{CS})$ (**2**) and **1** are displayed on the same chemical shift scale for ease of comparison. Immediately apparent are the marked variations present in the magnitudes of each of the three CS tensor principal

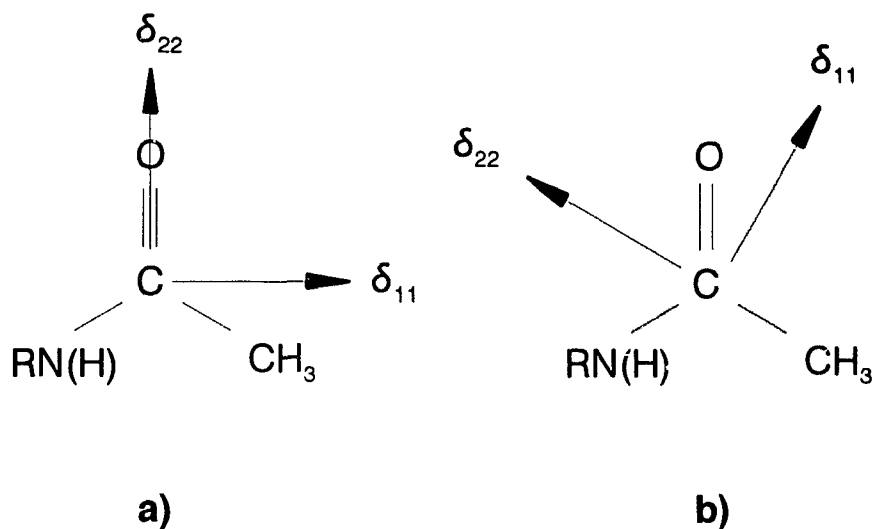


Figure 4.2 The two possible orientations of the carbonyl carbon CS tensor PAS for **1** consistent with the results of the analysis of the dipolar-chemical shift NMR spectra. For solution *b*), δ_{11} makes an angle of approximately 30° with respect to the C=O bond axis. The most shielded direction is perpendicular to the plane of the page for both solutions.

components; both the least shielded and intermediately shielded components are significantly more deshielded in the thioamide species while the most shielded component is notably more shielded. These variations lead to an overall increase of approximately 125 ppm in the span of the thioamide CS tensor. However, despite these significant differences, the magnitudes of the dipolar splittings, $\Delta\nu_{ii}$, exhibit striking similarities. This immediately suggests that the orientations of the carbon CS tensor PAS in these two compounds are analogous. It should be emphasized that the possibility of an exchange

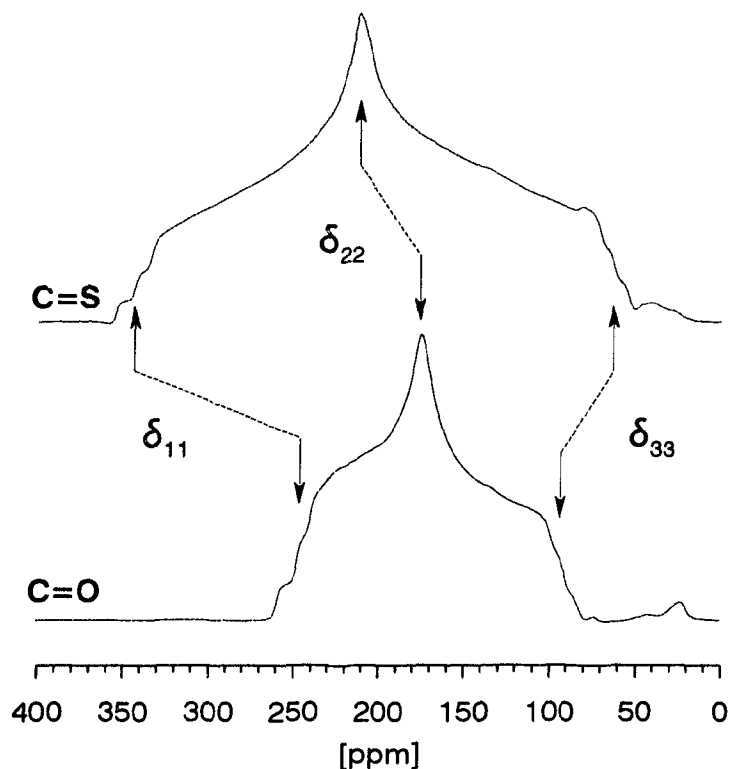


Figure 4.3 Experimental ^{13}C NMR spectra obtained at 9.4 T for static powder samples of **1** (lower) and **2** (upper). Features apparent in the experimental spectra in the region 10-80 ppm are due to carbon-13 nuclei present in natural abundance.

in orientation of the two in-plane CS tensor components, as speculated for the benzophenone/thiobenzophenone system (*139*), is readily rejected based on the relative magnitudes of the dipolar splittings, $\Delta\nu_{11}$ and $\Delta\nu_{22}$, observed for the thioamide. Such an exchange would result in larger dipolar splittings in the δ_{22} region of the powder pattern compared with the δ_{11} region, contrary to the experimentally observed result. The parameters used to calculate the ^{13}C NMR powder spectra of **2** at both applied fields employed in this study are as follows: $\delta_{11}=343 \pm 2$ ppm, $\delta_{22}=211 \pm 2$ ppm, $\delta_{33}=62 \pm$

2 pm, $\alpha = 29 \pm 3^\circ$, $\beta = 90 \pm 2^\circ$, $R_{\text{eff}} = 925 \pm 40$ Hz. The fact that $\beta = 90^\circ$ implies that the most shielded component, δ_{33} , lies normal to the S=C–N mirror plane, in analogy with the corresponding amide. Although there exists a two-fold ambiguity in defining the directions of the two in-plane tensor components, if one considers the results of *ab initio* MO carbon chemical shielding tensor calculations for several simple thioamides (*vide infra*), only the solution for which the intermediately shielded component is directed close to the C=S bond direction is reasonable.

4.4 Results and Discussion

Experimental Data. In Table 4.1, a summary of the experimental data obtained for all of the amides and thioamides investigated in this study is provided. The data indicate analogous trends to those outlined for **1** and **2** in §4.3. Each of the three principal components exhibits a significant sensitivity to sulfur substitution with both δ_{11} and δ_{22} more deshielded and δ_{33} more shielded in the thiocarbonyl fragment. In each case, the least shielded component shows the greatest sensitivity. Contrary to previous suggestions in the literature, the data indicate that the orientations of the carbon CS tensor PAS are analogous in that the intermediately shielded direction lies near the carbonyl or thiocarbonyl bond and the most shielded direction is normal to the amide/thioamide plane.

Also included in Table 4.1 are the results obtained from a literature survey concerning experimental data for the principal components of carbon CS tensors for the amide fragment. With the exception of one compound, acrylamide (*125*), all literature

Table 4.1 Principal Components and Orientations of the C=O and C=S Carbon CS Tensors in Several Amides and Thioamides^a

Compound	δ_{iso} (ppm)	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)	α (°)	β (°)	R_{eff} (Hz)	Ω (ppm)	ϕ^b (°)
4'-methoxyacetanilide- ¹³ C(CO)	171.3 ^c	246	177	92	29	90	895	154	—
4'-methoxythioacetanilide- ¹³ C(CS)	205.5 ^c	343	211	62	29	90	925	281	—
acetanilide- ¹⁵ N, ¹³ C(CO)	171.5 ^c	248	175	90	30	90	1230	158	+3
N-methylacetanilide- ¹⁵ N, ¹³ C(CO)	170.2 ^c	243	175	93	32	90	1250	150	−5
thioacetanilide- ¹⁵ N, ¹³ C(CS)	202	341	205	61	30	90	1257	280	—
acetamide- ¹³ C(CO)	176.9 ^c	243	202	86	38	90	888	157	−6
thioacetamide- ¹³ C(CS)	206	330	228	61	30	90	950	269	+3
benzophenone- ¹³ C(CO) ^d	200	272	229	99	—	—	—	173	—
thiobenzophenone- ¹³ C(CS) ^d	236	384	275	49	—	—	—	335	—
typical peptides	171(2)	243(4)	178(7)	93(4)	—	—	—	150(8)	—

^a The errors associated with the data are as follows: $\delta_{ii} \pm 2$ ppm, $\alpha \pm 3^\circ$, $\beta \pm 2^\circ$, and $R \pm 40$ Hz unless otherwise indicated in the text. ^b ϕ is the angle between δ_{22} and the carbonyl or thiocarbonyl bond axis. These angles have been calculated from the structural data available for acetanilide (155), N-methylacetanilide (156), acetamide (150), and thioacetamide (151). Positive angles refer to the side of the bond corresponding to the direction towards the nitrogen atom. ^c Obtained from CP/MAS solid-state NMR spectra. ^d From ref 139. Note that the chemical shifts reported in this study were with respect to liquid CS₂. These chemical shifts have been converted to the TMS scale using an isotropic shift for CS₂ of 192.8 ppm with respect to TMS. ^e From reference 119; these data are the average obtained from 23 different reference spectra of the amide fragment in peptides. The number in parentheses represents the standard deviation in the data.

values included in this survey pertain to peptides. The results obtained here for the carbon CS tensors of the amides are very similar to the average values obtained from the survey. The largest variation within each of the three principal components exists in the intermediate component, δ_{22} . In particular, it is evident that this component is significantly more deshielded in the primary amide, acetamide, compared with the other secondary and tertiary amides investigated. Although the complex task of definitively tracing the origins of such shielding trends is not directly feasible, it is worth mentioning that intermolecular influences will undoubtedly show wide variations within these compounds. For example, in acetamide (150) the oxygen atom is involved in two asymmetric hydrogen bonds with neighbouring molecules, unlike the situation for acetanilide where a single intermolecular hydrogen bond exists (155). Previous experimental and theoretical work (120c, 128, 132) has suggested the component of the carbonyl carbon CS tensor of amides most sensitive to hydrogen bonding to be the component lying nearest the carbonyl bond axis, δ_{22} . This component has been observed to become more deshielded with increasing hydrogen bond strength. Consequently, differences in the hydrogen bonding networks may partially account for the observed deshielding of δ_{22} in acetamide relative to the remaining compounds. Although N-H $\cdots$ S=C hydrogen bonds are expected to be weaker than corresponding N-H $\cdots$ O=C hydrogen bonds, the fact that thioacetamide and the thioacetanilides also display this trend is consistent with this argument and provides further support for the conclusion that the intermediately shielded component lies nearest the thiocarbonyl bond axis.

Theoretical Data. The results of the *ab initio* MO carbon chemical shielding

tensor calculations for several carbonyl and thiocarbonyl-containing molecules are presented in Table 4.2. The most significant aspect of these calculations concerns the orientation of the CS tensor PAS. For each molecule investigated, the calculations

Table 4.2 Calculated Carbonyl or Thiocarbonyl Carbon Chemical Shielding Tensors

Compound	σ_{11} (ppm)	σ_{22} (ppm)	σ_{33} (ppm)	σ_{iso} (ppm)	ϕ^c (°)
formaldehyde ^a	-111	-13	122	-1	0
thioformaldehyde ^a	-273	-109	173	-70	0
formamide ^a	-69	53	116	33	-6
thioformamide ^a	-211	-10	149	-24	0
acetamide monomer ^a	-97	13	114	10	+2
acetamide dimer ^a	-89	-3	115	8	+3
thioacetamide ^a	-241	-46	145	-47	+5
acetanilide ^b	-86	32	110	19	+3
<i>N</i> -methylacetanilide ^b	-79	14	116	17	+1

^a Calculations performed using the GIAO method and a Dunning TZP basis set. ^b Calculations performed using the IGLO method with the standard basis II. ^c ϕ is the angle between σ_{22} and the carbonyl or thiocarbonyl bond axis. Positive angles refer to the side of the bond that corresponds to the direction towards the nitrogen atom. In all cases, the most shielded direction is calculated to be perpendicular to the O=C-N or S=C-N plane.

predict an orientation such that the most shielded component lies normal to the X-C(O)-Y or X-C(S)-Y plane while the intermediately shielded component lies within this plane parallel to or nearest the carbonyl/thiocarbonyl bond axis. These results provide further conclusive evidence that the orientations of the carbon CS tensor PAS within the carbonyl

and thiocarbonyl fragments are qualitatively the same. Examination of the magnitudes of the principal components of the CS tensors for each of three carbonyl/thiocarbonyl pairs indicates trends analogous to those observed experimentally, although the calculated shielding differences are somewhat larger than observed. In each case, both the least shielded and intermediately shielded components are calculated to be more deshielded in the thiocarbonyls while the most shielded component is predicted to be more shielded. The fact that σ_{11} displays the greatest sensitivity to sulfur substitution in each case is also in agreement with the experimental data. Finally, in order to further investigate the influence of intermolecular effects (*e.g.* hydrogen bonding), the carbonyl carbon chemical shielding tensor has been calculated for the acetamide dimer which can be compared with the results for the monomeric species. Although the orientation of the PAS is relatively insensitive to hydrogen bonding, there are significant changes in the magnitudes of both the least shielded and particularly the intermediate components, with σ_{11} more shielded and σ_{22} more deshielded in the dimeric species. The most shielded component is found to be relatively insensitive. The fact that σ_{22} is calculated to be more deshielded in the hydrogen-bonded species is consistent with the aforementioned rationalization of the large deshielding observed for δ_{22} in the primary amides relative to the other secondary and tertiary amides.

Since several molecules have been investigated in this study both experimentally and theoretically, it is interesting to compare the results using these two different approaches. In Table 4.3, the calculated chemical shielding tensor data for these molecules have been converted to chemical shifts in order to facilitate a comparison

Table 4.3 Comparison of the Calculated and Experimental Carbonyl/Thiocarbonyl Carbon CS Tensors^a

Compound		δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)	δ_{iso} (ppm)	ϕ^d (°)
acetamide monomer	calc. ^b	283	173	72	176	+2
acetamide dimer	calc. ^b	275	189	71	179	+3
	exp.	243	202	86	177	-6
thioacetamide	calc. ^b	427	232	41	233	+5
	exp.	330	228	61	206	+3
acetanilide	calc. ^c	272	154	76	167	+3
	exp.	248	175	90	171	+3
<i>N</i> -methylacetanilide	calc. ^c	265	172	70	169	+1
	exp.	243	175	93	170	-5

^a The calculated shielding tensor principal components have been converted to chemical shifts using the absolute carbon chemical shielding in TMS, 186.0 ppm (157). ^b Calculations performed using the GIAO method and a Dunning TZP basis set. ^c Calculations performed using the IGLO method with the standard basis II. ^d ϕ is the angle between σ_{22} and the carbonyl or thiocarbonyl bond axis. Positive angles refer to the side of the bond that corresponds to the direction towards the nitrogen atom. In all cases, the most shielded direction is calculated to be perpendicular to the O=C-N or S=C-N plane.

with the experimental data. In general, the calculations are reasonably successful in predicting the orientations of the tensors as well as the magnitudes of the principal components. The most severe disagreement generally is observed in the least shielded component, δ_{11} , particularly for thioacetamide. There are several important points to be noted from the data in Table 4.3. Firstly, the incorporation of intermolecular effects into the calculation involving acetamide significantly improves the agreement between experiment and theory for both the least and intermediately shielded components,

suggesting the importance of hydrogen bonding in influencing the experimental CS tensor. Presumably, by incorporating each of the acetamide neighbors into the calculation to more accurately describe these intermolecular interactions, this agreement could be further improved. Secondly, note the very good agreement between experiment and theory in the isotropic chemical shift for each of the amides despite significant deviations in the tensor components. This result emphasizes the significance of including tensor principal components and not just isotropic values when reporting the results of shielding tensor computations. Thirdly, the results for acetanilide and *N*-methylacetanilide are very satisfactory considering the size of these molecules. It is noteworthy that the calculations predict a substantial intrinsic difference in the magnitudes of the intermediate components, δ_{22} , while experimentally these components are found to be identical. However, based on the results of the *ab initio* MO calculations concerning the influence of intermolecular hydrogen bonding, this result appears reasonable. More specifically, the differences in the magnitude of δ_{22} for isolated molecules of these amides may be masked experimentally by a deshielding of this component in acetanilide due to intermolecular hydrogen bonding. For the *N*-methyl derivative, such intermolecular interactions are impossible and hence the agreement between experiment and theory in this component is much improved. Finally, electron correlation has previously been found to be important in describing the carbonyl carbon shielding tensor (158) and is also anticipated to be important for the thiocarbonyl carbon shielding tensor. Therefore, the agreement between experiment and theory presumably could be enhanced by incorporating electron correlation into the MO calculations,

particularly for the least shielded component, δ_{11} .

Discussion. As alluded to in §2.3.1, in order to understand variations in chemical shifts, such as those observed for the carbonyl and thiocarbonyl carbon CS tensors, it is most important to focus on the paramagnetic contribution. Consider first the orientation of the carbonyl carbon CS tensor, which, as indicated, is qualitatively well established (134, 135). In agreement with the results obtained here, the most shielded direction is without exception found to lie normal to the amide plane. Thus, symmetry dictates that the paramagnetic shielding in this direction must originate from high-energy $\sigma \leftrightarrow \sigma^*$ mixing. The least shielded component, δ_{11} , lies within the amide plane and approximately perpendicular to the carbonyl bond axis and is thus influenced by $\sigma \leftrightarrow \pi^*$ as well as $\pi \leftrightarrow \sigma^*$ mixing. Finally, the intermediately shielded component, δ_{22} , also consistently lies within this plane but approximately parallel to the carbonyl bond axis. Based on symmetry considerations, $n \leftrightarrow \pi^*$ rotations contribute to the paramagnetic shielding in this direction. Furthermore, $\sigma \leftrightarrow \pi^*$ and $\pi \leftrightarrow \sigma^*$ mixing involving the C-C and C-N σ -bonds can also influence the paramagnetic shielding along the C=O bond axis. Before proceeding to discuss the results obtained for the thioamides, it is important to mention that, in general, a rationalization of a tensor orientation based exclusively upon energy differences between the contributing electronic states is not justifiable; the orientation of the carbonyl carbon CS tensor illustrates this point. Clearly, based solely on energy considerations, one would anticipate the least shielded direction (δ_{11}) to be along the CO bond as $n \leftrightarrow \pi^*$ mixing involves the HOMO-LUMO transition within the carbonyl fragment. The fact that the CO bond axis corresponds to the intermediately

shielded direction must primarily be a manifestation of the distance dependence of the paramagnetic shielding term. More specifically, the lone pair MO involved in the $n \leftrightarrow \pi^*$ mixing is essentially localized on the oxygen atom. Consequently, although important based on energy considerations, this influence is undoubtedly offset by an attenuation of the paramagnetic shielding along the carbonyl bond axis due to the r^{-3} dependence, resulting in this axis being the intermediately shielded direction.

The fact that both the experimental and theoretical results indicate analogous orientations of the carbon CS tensor PAS within the carbonyl and thiocarbonyl groups immediately indicates that the thiocarbonyl tensor orientation can be understood using electronic transition symmetry arguments as for the carbonyl fragment. An interesting finding of the present investigation is the fact that both of the in-plane CS tensor components, δ_{11} and δ_{22} , are more deshielded in the thioamides relative to the amides. Although the origin(s) of this deshielding cannot be traced with certainty from these results, it is worth emphasizing that both δ_{11} and δ_{22} are sensitive to the relative accessibility of the π^* MO given that the in-plane paramagnetic shielding is controlled by out-of-plane mixing. Consequently, the anticipated stabilization of the π -antibonding MO within the thioamides relative to the amides (142) must contribute, at least in part, to the observed in-plane deshielding. The result that the in-plane CS tensor component sensitive to the HOMO-LUMO $n \leftrightarrow \pi^*$ transition, δ_{22} , exhibits an apparent smaller sensitivity to sulfur substitution than that of the in-plane perpendicular component, δ_{11} , is not readily rationalized based exclusively on energy considerations. Once again, the distance dependence of the paramagnetic shielding term must, at least in part, be

responsible for this result. Clearly, the fact that the in-plane perpendicular component is influenced by mixing involving MO's that possess a relatively large amount of carbon $2p$ AO character must also contribute to the relative sensitivities of the two in-plane CS tensor components. Finally, it is interesting that the component perpendicular to the amide/thioamide plane is more shielded in the thioamides relative to the amides. However, given the multitude of plausible factors that could be influencing this trend, a definitive explanation unfortunately remains elusive.

In an effort to gain further information concerning the origins of the observed chemical shifts within the amides and thioamides, *ab initio* LORG (56) carbon chemical shielding tensor calculations have been performed for acetamide and thioacetamide. The advantage of this method over the GIAO approach lies not in accuracy but in the ability to provide insight into the electronic origins of the chemical shielding along a particular direction within a molecule. As mentioned in §2.3.1, the chemical shielding tensor is constructed as a series of localized bond contributions within the LORG formalism which facilitates a physical understanding of the computed tensors. The calculated LORG tensor components of acetamide and thioacetamide are provided in Table 4.4 and are found to be very similar to the results of the GIAO calculations (*cf.* Table 4.2). The tensor components have also been decomposed in Table 4.4 according to the contributions of the relevant valence MO's. The results predict that the least shielded components in these species are indeed dominated by the carbonyl/thiocarbonyl σ and π MO's (*i.e.* $\sigma \leftrightarrow \pi^*$ and $\pi \leftrightarrow \sigma^*$) and that the major contributor to the deshielding of δ_{11} in the thioamides relative to the amides involves the C-S σ -bond. As well, the major

Table 4.4 Decomposition of the Principal Components of the Carbon Chemical Shielding Tensors in Acetamide and Thioacetamide According to the Contributions of the Relevant Valence Localized MO's^a

Acetamide ^b				Thioacetamide ^c			
	σ_{11}	σ_{22}	σ_{33}		σ_{11}	σ_{22}	σ_{33}
C-O σ	-161	13	-33	C-S σ	-252	13	-11
C-O π	-45	20	3	C-S π	-80	15	1
O l.p.	-34	47	-12	S l.p.	-27	27	-10
C-N	-13	-95	-14	C-N	-8	-78	-9
C-C	-42	-120	-20	C-C	-68	-124	-5
other	201	147	193	other	198	110	189
total	-94	12	117	total	-237	-37	155

^a The calculations have been performed using the LORG method and a 6-311+G(3d,2p) basis set. ^b The results for the orientation of the chemical shielding tensor PAS in acetamide are analogous to the GIAO results (*cf.* Table 4.2). The angle ϕ is calculated to be $+4^\circ$. ^c The results for the orientation of the chemical shielding tensor PAS in thioacetamide are analogous to the GIAO results (*cf.* Table 4.2). The angle ϕ is calculated to be $+8^\circ$.

contributions to the paramagnetic shielding along the carbonyl/thiocarbonyl bond axis are associated with the C-C and C-N σ -bonds whereas the lone pair MO's of oxygen and sulfur make a shielding contribution in this direction. It should be mentioned that similar findings from an IGLO calculation on formaldehyde have previously been reported by Schindler and Kutzelnigg (159). However, it is interesting that the lone pair MO's are predicted to make the largest contribution to the deshielding observed for δ_{22} in

thioacetamide relative to acetamide. Finally, the calculations indicate that both the C-S and C-C σ -bonds are the primary sources of the shielding observed normal to the thioamide plane in thioacetamide relative to acetamide.

In light of the experimental findings for the thioamide CS tensors obtained here, the common interpretation of the decreased isotropic chemical shielding in the thiocarbonyl group relative to the carbonyl group in terms of decreased $n \rightarrow \pi^*$ energies (137) must be revoked; it appears a decrease in energy of $\sigma \rightarrow \pi^*$ transitions is the predominant cause of this deshielding. This result demonstrates the dangers inherent in the familiar practice of deriving relationships between HOMO-LUMO excitation energies and *isotropic* chemical shifts and emphasizes the sensitivity of paramagnetic shielding to factors other than energy differences. Similar conclusions have recently been forwarded for the non-importance of $n \rightarrow \pi^*$ transition energies in dictating carbonyl isotropic chemical shifts (160). Clearly, regardless of the success of HOMO-LUMO excitation energy and isotropic CS correlations, projecting such findings to rationalize isotropic chemical shift differences is completely unsubstantiated in the absence of information concerning trends in the individual CS tensor components as well as the orientation of these components in the molecular frame.

In closing, some comments concerning the results of the benzophenone/thiobenzophenone investigation (139) are in order. The three principal components of the carbonyl/thiocarbonyl carbon CS tensors measured by Kempf *et al.* for these compounds are provided in Table 4.1. The tensor components show analogous trends to those observed within the amides and thioamides investigated here. It appears that the

origin of the conclusion of this paper that the two in-plane tensor components exchange orientation was based on the assumption that the CS tensor components lying along the C=O and C=S bonds should be inversely proportional to the $n \rightarrow \pi^*$ excitation energies within these compounds ($26,800\text{ cm}^{-1}$ in benzophenone and $16,400\text{ cm}^{-1}$ for thiobenzophenone) (139). Since δ_{22} was known to lie along the C=O bond in benzophenone (143), this relationship is most closely observed with δ_{11} oriented along the C=S bond in thiobenzophenone. However, based on the results of the present investigation and the discussion in the preceding paragraph, such an assumption is clearly not valid.

4.5 Conclusions

In this chapter, it has been shown how the combination of *experimental* solid-state NMR studies and *theoretical* MO calculations can be an invaluable tool to obtain detailed insight into CS tensors and their structural origins. Clearly, in the absence of either of these two complementary techniques, the conclusions of this investigation would be constructed upon a weakened foundation. The most significant finding of this study is that for the first time, it has been shown that the orientations of the carbonyl and thiocarbonyl carbon CS tensors are qualitatively the same. This information, in combination with the trends observed in the magnitudes of the CS tensor principal values, has provided valuable insight into the origins of the deshielding observed in $\delta_{\text{iso}}(^{13}\text{C})$ in the C=S fragment relative to C=O. The fact that variations in $n \rightarrow \pi^*$ transition energies are not responsible for this deshielding corrects earlier misconceptions in the

literature. As well, the results for the shielding tensor calculations in this study illustrate the importance of providing the calculated magnitudes of the three tensor principal components rather than just the isotropic value. Many authors in the past have been guilty of simply tabulating calculated isotropic shieldings, making it difficult to evaluate the success of these calculations when comparing with experimental data. Finally, this study is illustrative of the general theme of this thesis in that none of this valuable information would have been obtainable by simply looking at isotropic chemical shifts and not examining the full CS tensor.

Chapter 5

Concluding Remarks

In this thesis, valuable information concerning the fundamental origins of anisotropic nuclear spin interactions in solids has been acquired through the use of solid-state NMR spectroscopy and theoretical techniques. This information has been afforded by detailed investigations into the orientation-dependent nature of these interactions rather than the more familiar orientational average measured in solution. The results of this work will have far-reaching implications in terms of how chemists tend to "visualize" these interactions. For example, undoubtedly the most reliable evidence to date for an anisotropic J coupling has been presented in this thesis. The fact that the ^{199}Hg - ^{31}P J tensors in mercury-phosphine complexes exhibit such large anisotropies provides proof that non-Fermi contact mechanisms make substantial contributions to this coupling. For decades, chemists have attempted to interpret such couplings, and indeed metal-phosphorus couplings in general, in terms of the FC mechanism alone. In light of the findings of this thesis, these approaches may need to be re-evaluated. As well, for the first time, evidence has been provided as to the origins of the large differences in isotropic carbon chemical shifts within the carbonyl and thiocarbonyl groups. Besides correcting earlier misconceptions in the literature, this study has also illustrated the dangers inherent in interpreting chemical shifts in the absence of information concerning the three-dimensional nature of this interaction.

The research in this thesis could potentially be extended in a variety of different

directions. As for the work on indirect spin-spin couplings, it is clear that we have "barely scratched the surface" in terms of understanding the structural factors dictating the anisotropic nature of **J**. For example, how does multiple bonding influence the **J** tensor? How would a **J** tensor be oriented for two coupled nuclei separated by more than one bond? These and other unanswered yet fundamental questions need to be addressed before our understanding can be improved. Therefore, further reliable systematic studies of **J** tensors are warranted. It would also be useful to investigate the proposal by Power and Wasylshen that platinum-phosphorus *J* couplings possess large anisotropies (84) by performing a single-crystal study for one or more of these complexes. The work of Olivieri concerning anisotropic copper-phosphorus *J* couplings also should be explored further (118). Finally, it would also be informative to examine metal couplings involving nuclei other than phosphorus. For example, there have been reports that ^{199}Hg - ^{13}C *J* couplings possess considerable anisotropic character (161).

The work involving the carbon chemical shift tensors in C=O and C=S groups could be extended by investigating the C=Se fragment, for which the carbon nucleus is even more deshielded than in thiocarbonyls. Once again, this deshielding has been rationalized in the past as due to variations in longest wavelength excitation energies based on correlations involving the *isotropic* carbon chemical shift (137b). Thus, it would be instructive to perform an investigation into the carbon chemical shift *tensor* of the C=Se fragment taking the approach adopted in Chapter 4 of this thesis.

Appendix I

Rotational Transformations

A frequent task when analyzing solid-state NMR line shapes involves transformation of a vector from one reference frame to another. As the necessary concepts are an integral part of the single-crystal experiment as well as the computer code presented in Appendix II, a brief review is provided here for the sake of completeness. For a more detailed analysis, the reader is referred to the text by Graybeal (162). Central to this discussion is the "sense" or "handedness" of a Cartesian axis system, defined in Figure A1.1. In this appendix, reference frames are assumed to

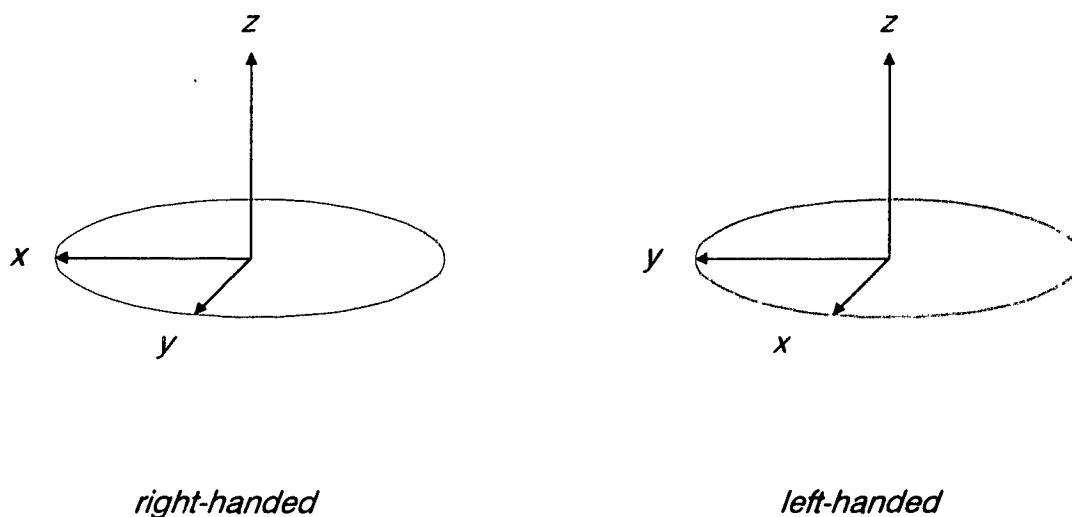


Figure A1.1 Diagram illustrating the difference between a right-handed and left-handed Cartesian coordinate system. The handedness can be determined by applying the right-hand thumb rule. For example, pointing the right thumb in a direction corresponding to the positive x axis transforms $+y$ into $+z$ for the right-handed reference frame and $+y$ into $-z$ for the left-handed reference frame.

be orthogonal and right-handed.

Consider a vector, $\mathbf{M}$, in a Cartesian axis system, (x, y, z) , so that:

$$\mathbf{M} = M_x + M_y + M_z \quad (\text{A1.1})$$

Our job is to transform $\mathbf{M}$ to a second Cartesian axis system, (a, b, c) , which has a common origin but has been rotated relative to (x, y, z) . This transformation can be accomplished using direction cosines, which enable projection of each component of $\mathbf{M}$ in (x, y, z) onto each "new" axis in (a, b, c) . For example, M_a is found by projecting M_x , M_y , and M_z onto the a axis and summing:

$$M_a = \cos \Phi_{ax} M_x + \cos \Phi_{ay} M_y + \cos \Phi_{az} M_z \quad (\text{A1.2})$$

In the above equation, Φ_{ai} represents the angle between the a axis and the appropriate axis in (x, y, z) . The $\cos \Phi_{ai}$ are the direction cosines which enable projection of the i th component of $\mathbf{M}$ onto the a axis. In an analogous manner, the other two components of $\mathbf{M}$ in (a, b, c) are as follows:

$$M_b = \cos \Phi_{bx} M_x + \cos \Phi_{by} M_y + \cos \Phi_{bz} M_z \quad (\text{A1.3})$$

$$M_c = \cos \Phi_{cx} M_x + \cos \Phi_{cy} M_y + \cos \Phi_{cz} M_z \quad (\text{A1.4})$$

Equations A1.2 - A1.4 can be conveniently represented in vector-matrix notation as:

$$\begin{pmatrix} M_a \\ M_b \\ M_c \end{pmatrix} = \begin{pmatrix} \cos \Phi_{ax} & \cos \Phi_{ay} & \cos \Phi_{az} \\ \cos \Phi_{bx} & \cos \Phi_{by} & \cos \Phi_{bz} \\ \cos \Phi_{cx} & \cos \Phi_{cy} & \cos \Phi_{cz} \end{pmatrix} \begin{pmatrix} M_x \\ M_y \\ M_z \end{pmatrix} \quad (\text{A1.5})$$

The direction cosine matrix in eq. A1.5 is known as a rotation matrix, $\mathbf{R}$, which rotates a vector from one coordinate system to another:

$$\mathbf{M}(a, b, c) = \mathbf{R} \mathbf{M}(x, y, z) \quad (\text{A1.6})$$

A convenient method of treating vector rotations is through the use of Euler angles (α, β, γ) . These angles represent a set of three rotations which define the orientation of some axis system relative to another. Once the Euler angles have been established, the appropriate rotation matrix can be readily calculated. In order to define the Euler angles relating (a, b, c) to (x, y, z) , one starts with the two axis systems in coincidence. The angle α corresponds to a rotation about the c axis so that:

$$\mathbf{R}_c(\alpha) = \begin{pmatrix} \cos \alpha & \sin \alpha & 0 \\ -\sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (\text{A1.7})$$

The angle β represents a rotation about the new b axis, b' , generated by the initial α rotation:

$$\mathbf{R}_{b'}(\beta) = \begin{pmatrix} \cos \beta & 0 & -\sin \beta \\ 0 & 1 & 0 \\ \sin \beta & 0 & \cos \beta \end{pmatrix} \quad (\text{A1.8})$$

Finally, the Euler angle γ corresponds to a rotation about the new c axis, c'' , generated by the initial two rotations:

$$\mathbf{R}_{c''}(\gamma) = \begin{pmatrix} \cos \gamma & \sin \gamma & 0 \\ -\sin \gamma & \cos \gamma & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (\text{A1.9})$$

Therefore, rotation of a vector $\mathbf{M}$ from (x, y, z) to (a, b, c) is accomplished by:

$$\mathbf{M}(a, b, c) = \mathbf{R}_{c''}(\gamma) \mathbf{R}_{b'}(\beta) \mathbf{R}_c(\alpha) \mathbf{M}(x, y, z) = \mathbf{R} \mathbf{M}(x, y, z) \quad (\text{A1.10})$$

where:

$$\mathbf{R} = \begin{pmatrix} \cos \gamma \cos \beta \cos \alpha & \cos \gamma \cos \beta \sin \alpha & -\cos \gamma \sin \beta \\ -\sin \gamma \cos \beta \cos \alpha & -\sin \gamma \cos \beta \sin \alpha & \sin \gamma \sin \beta \\ \sin \beta \cos \alpha & \sin \beta \sin \alpha & \cos \beta \end{pmatrix} \quad (\text{A1.11})$$

Appendix II

Listing of "C" Computer Code For Calculation of the ^{31}P NMR

Line Shape for a Static Powder Sample of $\text{Hg}(\text{PPh}_3)_2(\text{NO}_3)_2$

Although a wide variety of computer simulation programs are available in this laboratory for calculating NMR line shapes, the ^{31}P NMR spectrum for a static powder sample of the 1:2 mercury-phosphine complex, $\text{Hg}(\text{PPh}_3)_2(\text{NO}_3)_2$, was not treatable with any of the existing software. Thus, a program was developed and employed in Chapter 3 of this thesis which handles a general three-spin *ABX* spin system. Included here is a complete listing of the computer code. However, I first wish to acknowledge the assistance of Dr. Klaus Eichele in developing this software. Klaus performed the translation of the *POWDER* routine from FORTRAN-77 code to the C language and also kindly provided me with a routine for convoluting the calculated line shapes.

The program has been written using the Borland C developers language and consists of four distinct modules. The *SETUP* module assigns the spin-system parameters and also incorporates the expressions for the frequencies and intensities of the four transitions for an *AB* spin pair (40, 103, 163):

$$\nu_1 = \nu_0 + \frac{D}{2} + \frac{A}{2} \quad I_1 = 1 - \frac{B}{D} \quad (\text{A2.1})$$

$$\nu_2 = \nu_0 + \frac{D}{2} - \frac{A}{2} \quad I_2 = 1 + \frac{B}{D} \quad (\text{A2.2})$$

$$\nu_3 = \nu_0 - \frac{D}{2} + \frac{A}{2} \quad I_3 = 1 + \frac{B}{D} \quad (\text{A2.3})$$

$$\nu_4 = \nu_0 - \frac{D}{2} - \frac{A}{2} \quad I_4 = 1 - \frac{B}{D} \quad (\text{A2.4})$$

where $\nu_0 = (\nu_A + \nu_B)/2$, ν_A and ν_B are the chemical shifts of the two nuclei (frequency units), and

$$D = \sqrt{\Delta\nu^2 + B^2} \quad (\text{A2.5})$$

$$B = J + \frac{R_{DD}}{2} (3\cos^2\theta - 1) \quad (\text{A2.6})$$

$$A = J - R_{DD} (3\cos^2\theta - 1) \quad (\text{A2.7})$$

In the above equations, $\Delta\nu = \nu_A - \nu_B$, R_{DD} is the dipolar coupling constant (*cf.* eq. 2.13), and θ is the angle between the internuclear vector and the external magnetic field. The *POWDER* module performs the powder averaging using the routine of Alderman *et al.* (99). The program is designed to perform this averaging in some arbitrary reference frame and so the relative orientations for each of the relevant interaction tensors with respect to this reference frame must be specified by the user within *SETUP*. This approach is convenient, particularly when working with single-crystal data, as the powder averaging can be performed within the NMR cube frame and the single-crystal data can

then be used directly. Note that the program assumes **J** to be axially symmetric and aligned with **D**. The *BROADEN* module convolutes the calculated line shape with either a Lorentzian or Gaussian line broadening function or any mixture of the two. Finally, the *GRAPH* module has been included so that the calculated spectrum can be immediately displayed on-screen.

```

/*****
MODULE      :      POWDER.H
PURPOSE      :      This header file contains definitions of two very
                      important structures to this project; SpecParam and
                      SpinSysStd.  As well, constants are defined and
                      module functions are prototyped.

DATE        :      February, 1994
*****/

```

```
// libraries used in the project
```

```

#include      <stdio.h>
#include      <conio.h>
#include      <stdlib.h>
#include      <math.h>
#include      <dos.h>
#include      <string.h>
#include      <mem.h>
#include      <graphics.h>

```

```
#define NNTT 32
```

```
#define DEG 0.017453292519943 // Convert between radians and degrees
```

```

/* -----
   structure SpecParam holds various parameters defining the calculated spectrum
   -----*/

```

```

struct SpecParam
{
    unsigned int    NSite;        // No. of sites present
    struct SpinSysStd *First;      // Pointer to 1st spin system
    struct SpinSysStd *Curr;      // Pointer to current spin system
    struct SpinSysStd *Last;      // Pointer to last spin system
    float           *Spectrum;    // Pointer to spectrum
    unsigned int    NT;          // No. of intersections for POWDER
    unsigned int    Points;      // No. of points (>= 4)
    float           Fnew;        // Larmor frequency
    float           HiFreq;      // High-frequency limit
    float           LoFreq;      // Low-frequency limit
    float           Width;       // Width of spectrum (Hi - Lo)
    float           Incr;        // Digital resolution
    float           Max;         // Maximum intensity in spectrum
    float           Min;         // Minimum intensity in spectrum
};

```

```

/* -----
   structure SpinSysStd holds various parameters defining a general spin system
   -----*/

```

```

-----*/
struct SpinSysStd
{
    float    Relin;        // Relative intensity of site.
    float    Prob;         // Probability of transition.
    float    ASpin;        // Spin of nucleus observed (A).
    float    AState;       // Spin state of A.
    float    AS11;         // Delta-11 of A.
    float    AS22;         // Delta-22 of A.
    float    AS33;         // Delta-33 of A.
    float    AAlpha;       // Euler Angles for A shift PAS
    float    ABeta;        // with respect to NMR cube frame
    float    AGamma;
    float    BSpin;        // Spin of nucleus B
    float    BState;       // Spin state of B
    float    BS11;         // Delta-11 of B.
    float    BS22;         // Delta-22 of B.
    float    BS33;         // Delta-33 of B.
    float    BAlpha;       // Euler Angles for B shift PAS
    float    BBeta;        // with respect to NMR cube frame
    float    BGamma;
    float    PF;           // Homo-/heteronuclear factor.
    float    D;            // P-P Dipolar coupling constant.
    float    CJ;           // P-P Indirect coupling constant.
    float    DelJ;         // Anisotropy in P-P J.
    float    CAlpha;       // Polar angles for P-P Dipolar Vector
    float    CBeta;        // with respect to NMR cube frame
    float    DAlpha;       // Polar angles for P-Hg Dipolar Vector
    float    DBeta;        // with respect to NMR cube frame
    float    EAlpha;       // Polar angles for other P-Hg Dipolar
    float    EBeta;        // Vector with respect to NMR cube frame
    float    CState;       // Hg-199 spin state
    float    het_j;        // P-31 Hg-199 J coupling constant
    float    het_rdd;      // P-31 Hg-199 Dipolar coupling constant
    float    het_del_j;    // P-31 Hg-199 Anisotropy in J
};

/* -----
                        prototypes for functions used in this project
-----*/

int Powder( struct SpecParam *Simul, int (*Line)( float cosx,
float cosy,
float cosz,
float *freq,
float *amp,

```



```

                                struct SpecParam *Simul));
int Tent( float freq1, float freq2, float freq3, float amp, struct SpecParam *Simul);
int Line1(    float cosx, float cosy, float cosz,
              float *freq, float *amp, struct SpecParam *Simul );
int Line2(    float cosx, float cosy, float cosz,
              float *freq, float *amp, struct SpecParam *Simul );
int Convolute( float *Spec, int Points, float _finc);
int GetMinMax( float *spec, float *max, float *min, int points);
int Display( struct SpecParam *Simul);
void rotate_( float *cosines, const float *older, float *newer);

```

```

/*****
MODULE      :      SETUP.CPP
PURPOSE      :      The SETUP module dynamically allocates memory
                      for spin system and spectral parameters as well as
                      spectral intensity data. After assigning the relevant
                      parameters, powder averaging is then initiated. The
                      module also contains functions for calculating
                      frequency and intensity data as a function of the
                      orientation generated within POWDER as well as a
                      routine for vector rotations.

DATE          :      February, 1994
PROGRAMMER:      Mike Lumsden
*****/

```

```
#include "powder.h"
```

```

void main()
{
int          i, j, k;
float         *Spec;           // pointer to spectral intensity data
struct SpecParam *Simul;       // pointer to spectral parameters
struct SpinSysStd *SpinSys1, *SpinSys2; // pointers to two spin systems
FILE          *fp;            // file pointer for output of data
char          FileName[40];
char          Root[15] = "1to2400.txt";
int           count=0;
float         upper, lower;    // spectral limits in ppm
int           (*Line)(float cosx, float cosy, float cosz, float *freq, float *amp,
                      SpecParam *Simul); // function pointer to appropriate line
                                              // equation

```

```
clrscr();
```

```

/* -----
                        get and zero memory to hold spectral parameters
----- */

```

```

Simul = (struct SpecParam *) malloc(sizeof(struct SpecParam));
if (Simul == NULL)
{
    printf("Memory Allocation Failed!!\n"
           "Terminating execution!!\n\a");
    sleep(2);
    exit(1);
}
setmem(Simul, sizeof(struct SpecParam), NULL); // zero memory

```

```

/* -----
    get and zero memory to hold parameters for spin systems
-----*/

// the first record handles the P-P AB spin system
SpinSys1 = (struct SpinSysStd *) malloc(sizeof(struct SpinSysStd));
if (SpinSys1 == NULL)
{
    printf("Memory Allocation Failed!!");
    exit(1);
}
setmem(SpinSys1, sizeof(struct SpinSysStd), NULL);    // zero memory

// the second record handles the P-Hg-P ABX spin system
SpinSys2 = (struct SpinSysStd *) malloc(sizeof(struct SpinSysStd));
if (SpinSys2 == NULL)
{
    printf("Memory Allocation Failed!!");
    exit(1);
}
setmem(SpinSys2, sizeof(struct SpinSysStd), NULL);    // zero memory

/* -----
    get and zero memory to hold spectral intensity data
-----*/

Spec = (float *) malloc((Simul->Points)*(sizeof(float)));
if (Spec == NULL)
{
    printf("Memory Allocation Failed!!\n"
           "Terminating execution!!\n\a");
    sleep(2);
    exit(1);
}
Simul->Spectrum = Spec;
setmem(Spec, (Simul->Points)*sizeof(float), NULL);    // zero memory

/* -----
    assign spectral parameters
-----*/

Simul->First      = SpinSys1;
Simul->Curr       = SpinSys1;
Simul->Last       = SpinSys2;
Simul->Points     = 4096;           // spectral points
Simul->Fnew       = 81.033;        // observe Larmor frequency
upper            = 150.0;          // high-frequency limit of spectrum (ppm)
lower            = -50.0;          // low-frequency limit of spectrum (ppm)
Simul->HiFreq     = Simul->Fnew * upper;    // convert to Hz
Simul->LoFreq     = Simul->Fnew * lower;

```

```
/* -----
      assign parameters for first spin system (P-P)
      these are the parameters obtained from the single-crystal study
```

SpinSys1->Relin	=	100.0-16.84;	SpinSys1->Prob	=	100.0;
SpinSys1->AS11	=	71.0;	SpinSys1->AS22	=	32.0;
SpinSys1->AS33	=	14.5;	SpinSys1->AAAlpha	=	75.48;
SpinSys1->ABeta	=	35.90;	SpinSys1->AGamma	=	165.60;
SpinSys1->BS11	=	71.0;	SpinSys1->BS22	=	32.0;
SpinSys1->BS33	=	14.5;	SpinSys1->BAAlpha	=	12.11;
SpinSys1->BBeta	=	134.03;	SpinSys1->>BGamma	=	355.72;
SpinSys1->D	=	220.2;	SpinSys1->CJ	=	250.0;
SpinSys1->DelJ	=	0.0;	SpinSys1->CAAlpha	=	155.91;
SpinSys1->CBeta	=	13.44;			

```

/* -----
      assign parameters for second spin system (P-Hg-P)
      these are the parameters obtained from the single-crystal study

```

SpinSys2->Relin	=	16.84;	SpinSys2->Prob	=	100.0;
SpinSys1->AS11	=	71.0;	SpinSys1->AS22	=	32.0;
SpinSys1->AS33	=	14.5;	SpinSys1->AAAlpha	=	75.48;
SpinSys1->ABeta	=	35.90;	SpinSys1->AGamma	=	165.60;
SpinSys1->BS11	=	71.0;	SpinSys1->BS22	=	32.0;
SpinSys1->BS33	=	14.5;	SpinSys1->BAAlpha	=	12.11;
SpinSys1->BBeta	=	134.03;	SpinSys1->BGamma	=	355.72;
SpinSys1->D	=	220.2;	SpinSys1->CJ	=	250.0;
SpinSys1->DelJ	=	0.0;	SpinSys1->CAAlpha	=	155.91;
SpinSys1->CBeta	=	13.44;	SpinSys2->het_j	=	5550.0;
SpinSys2->het_rdd	=	599.0;	SpinSys2->het_del_j	=	4000.;
SpinSys2->DAAlpha	=	251.5;	SpinSys2->DBeta	=	158.4;
SpinSys2->EAlpha	=	199.3;	SpinSys2->EBeta	=	32.3;
SpinSys2->BSpin	=	0.5;			

```
/* -----
spectrum calculation starts here
```

```

Simul->Curr = SpinSys1;      // start with P-P AB spin system
Line = Line1;              // assign appropriate line function

```

```

// this double loop powder averages each of the four transitions for the AB spin system
for (i=-1; i <= 1; i+=2)
{
    for (j=-1; j <= 1; j+=2)
    {
        SpinSys1->AState = i;           // used in line1 function
        SpinSys1->BState = j;           // used in line1 function
        count++;
        printf("Powder Averaging Transition #%1d\n", count);
        Powder(Simul,Line);             // do powder averaging
    }
}

Simul->Curr = SpinSys2;                 // now do the P-Hg-P ABX spin system
Line = Line2;                          // select appropriate line function
// now need a triple loop to calculate Hg-199 satellite spectra; a double loop for each
// Hg-199 spin state
for(k = -1; k <= 1; k+=2)
{
    SpinSys2->CState = 0.5*k;           // Hg-199 spin state
    for (i=-1; i <= 1; i+=2)
    {
        for (j=-1; j <= 1; j+=2)
        {
            SpinSys2->AState = i;       // used in line2 function
            SpinSys2->BState = j;       // used in line2 function
            count++;
            printf("Powder Averaging Transition #%1d\n", count);
            Powder(Simul,Line);         // do powder averaging
        }
    }
}

// broaden the spectrum
Convolute(Spec, Simul->Points, Simul->Incr);

// write calculated spectrum to an output file
sprintf(FileName, "%s", Root);
fp = fopen(FileName,"w");
fprintf(fp, " %d\n", Simul->Points);
fprintf(fp, " %f\n", Simul->Fnew);
fprintf(fp, " %f\n", Simul->Incr);
fprintf(fp, " %f\n", Simul->HiFreq);
fprintf(fp, " %f\n", Simul->LoFreq);

```

```

for (i=0; i< Simul-> Points; i++)
    fprintf(fp, "%f\n", Spec[i]);
fclose(fp);

```

```

// scan spectral intensity data for maxima and minima for formatting output to screen
GetMinMax(Spec, &(Simul-> Max), &(Simul-> Min), Simul-> Points);

```

```

// display calculated spectrum
Display(Simul);
}

```

```

/* -----
                        FUNCTION LINE1()

```

This function is called by the powder routine, which passes direction cosines of the magnetic field vector relative to the NMR cube frame in this case, (cosx, cosy, cosz). The function then rotates the field vector to the PAS of the appropriate interaction tensor before calculating the frequency and intensity data. These data are assigned to *freq and *amp, respectively. LINE(1) handles the *AB* part of the powder pattern.

```

-----*/

```

```

int Line1(    float cosx, float cosy, float cosz,
              float *freq, float *amp, struct SpecParam *Simul)
{
    float Anu, Bnu, Del, Avnu, Afac, Bfac, Dfac, nu, inten, d, cj, delj;
    float asina, acosa;
    float bsing, bcosg;
    struct SpinSysStd *SpinSys;
    float old[3], newer[3], angles[3];

```

```

    SpinSys = Simul-> Curr;
    old[0] = cosx;    old[1] = cosy;    old[2] = cosz;

```

```

/* -----
                        first get resonance frequency for A
-----*/

```

```

// rotate field into PAS of shielding tensor for nucleus A
// rotated eigenvectors are stored in newer
// appropriate Euler angles are stored in angles
angles[0] = (SpinSys-> AAlpha)*DEG;    // convert Euler angles to radians
angles[1] = (SpinSys-> ABeta)*DEG;
angles[2] = (SpinSys-> AGamma)*DEG;
rotate_f(angles, old, newer);          // do rotation
// calculate frequency for nucleus A
Anu = Simul-> Fnew*(    newer[0]*SpinSys-> AS11*newer[0] +

```

```

newer[1]*SpinSys->AS22*newer[1]+
newer[2]*SpinSys->AS33*newer[2] );

/* -----
               now do the same thing for nucleus B
-----*/

// rotate field into PAS of shielding tensor for nucleus B
// rotated eigenvectors are stored in newer
// appropriate Euler angles are stored in angles
angles[0]= (SpinSys->BAlpha)*DEG;    // convert Euler angles to radians
angles[1]= (SpinSys->BBeta)*DEG;
angles[2]= (SpinSys->>BGamma)*DEG;
rotate_f(angles,old,newer);          // do rotation
// calculate frequency for nucleus B
Bnu = Simul->Fnew*(    newer[0]*SpinSys->BS11*newer[0]+
                      newer[1]*SpinSys->BS22*newer[1]+
                      newer[2]*SpinSys->BS33*newer[2] );

/* -----
               now get angle between field and P-P dipolar vector
-----*/

// rotate field into PAS of P-P dipolar tensor
// rotated eigenvectors are stored in newer and used in AB expressions
// appropriate Euler angles are stored in angles
angles[0] = (SpinSys->CAlpha)*DEG;    // convert Euler angles to radians
angles[1] = (SpinSys->CBeta)*DEG;
angles[2] = 0;
rotate_f(angles,old,newer);          // do rotation

/* -----
               calculate frequency and intensity data using eqs. A2.1-A2.7
-----*/

//  $\nu_o$  in eqs. A2.1-A2.4
Aanu = (Anu + Bnu)*0.5;
// A in eq. A2.7
Afac = (SpinSys->CJ) - ((SpinSys->D)-(SpinSys->DelJ)/3)*
        (3.0*newer[2]*newer[2] - 1);

// B in eq. A2.6
Bfac = (SpinSys->CJ) + 0.5*(((SpinSys->D)-(SpinSys->DelJ)/3)*
        (3.0*newer[2]*newer[2] - 1));
//  $\Delta\nu$  in eq. A2.5
Del = fabs(Anu-Bnu);
// D in eq. A2.5

```

```

Dfac  =      sqrt( Del*Del + Bfac*Bfac );

// calculate frequency and intensity using eqs. A2.1-A2.4. Which transition is calculated
// is controlled by the double loop within main() and the values of SpinSys->AState and
// SpinSys->BState
nu     =      Avnu + 0.5*Dfac*(SpinSys->AState) + 0.5*Afac*(SpinSys->BState);
inten  =      (1 + ((Bfac/Dfac)*(SpinSys->AState)*
                  (SpinSys->BState)*(-1.0))) * (SpinSys->Prob) * (SpinSys->Relin);

*freq  =      nu;
*amp    =      inten;
return 0;
}

```

```

/* -----
                        FUNCTION LINE2()

```

LINE2() handles the Hg-199 satellite spectra or the *ABX* part of the powder pattern. This function is very similar to LINE1() and therefore is not documented as extensively as LINE1() was. Only the important differences will be indicated

```

-----*/
int Line2(      float cosx, float cosy, float cosz,
                float *freq, float *amp, struct SpecParam *Simul)
{
float Anu, Bnu, Del, Avnu, Afac, Bfac,Dfac, nu, inten;
float asina, acosa;
float bsin, bcos, relin;
struct SpinSysStd *SpinSys;
float old[3], newer[3], angles[3];

SpinSys = Simul->Curr;
relin  = (SpinSys->Relin)/(2*SpinSys->BSpin + 1);
old[0] = cosx;      old[1] = cosy;      old[2] = cosz;

angles[0]= (SpinSys->AAlpha)*DEG;
angles[1]= (SpinSys->ABeta)*DEG;
angles[2]= (SpinSys->AGamma)*DEG;
rotate_f(angles,old,newer);
Anu = Simul->Fnew*(      newer[0]*SpinSys->AS11*newer[0]+
                        newer[1]*SpinSys->AS22*newer[1]+
                        newer[2]*SpinSys->AS33*newer[2]      );

angles[0]= (SpinSys->BAlpha)*DEG;
angles[1]= (SpinSys->BBeta)*DEG;

```



```

angles[2]= (SpinSys->BGamma)*DEG;
rotate_f(angles,old,newer);
Bnu = Simul->Fnew*(    newer[0]*SpinSys->BS11*newer[0]+
                      newer[1]*SpinSys->BS22*newer[1]+
                      newer[2]*SpinSys->BS33*newer[2]    );

/* -----
The main difference between LINE1() and LINE2() lies here. The following code
calculates an effective resonance frequency for A and B, modified due to spin-spin
coupling with the Hg-199 nucleus. This is so an effective chemical shift difference can
be used in the expressions for the AB transitions for both of the Hg-199 satellites.
-----*/

// rotate field into PAS of one P-Hg effective coupling tensor
// appropriate Euler angles are stored in angles
angles[0]= (SpinSys->DAlpha)*DEG;           // convert Euler angles to radians
angles[1]= (SpinSys->DBeta)*DEG;
angles[2]= 0;
rotate_f(angles,old,newer);                // perform rotation
// calculate modified resonance frequency for nucleus A
Anu += ((SpinSys->CState)*((SpinSys->het_rdd) -
((SpinSys->het_del_j)/3.0))*(3*newer[2]*newer[2] - 1.0)) -
(SpinSys->CState)*(SpinSys->het_j);

// rotate field into PAS of the other P-Hg effective coupling tensor
// appropriate Euler angles are stored in angles
angles[0]= (SpinSys->EAlpha)*DEG;           // convert to radians
angles[1]= (SpinSys->EBeta)*DEG;
angles[2]= 0;
rotate_f(angles,old,newer);                // perform rotation
// calculate modified resonance frequency for nucleus B
Bnu += ((SpinSys->CState)*((SpinSys->het_rdd) -
((SpinSys->het_del_j)/3.0))*(3*newer[2]*newer[2] - 1.0)) -
(SpinSys->CState)*(SpinSys->het_j);

/* -----
                        everything from here on is the same as in LINE1()
-----*/

angles[0]= (SpinSys->CAlpha)*DEG;
angles[1]= (SpinSys->CBeta)*DEG;
angles[2]= 0;
rotate_f(angles,old,newer);

Avnu = (Anu + Bnu)*0.5;
Afac = (SpinSys->CJ) - ((SpinSys->D)-(SpinSys->DelJ)/3)*

```



```
// calculate Z component of rotated vector
newer[2]= ( sin(cosines[1])*cos(cosines[0]) ) * older[0];
newer[2]+= ( sin(cosines[1])*sin(cosines[0]) ) * older[1];
newer[2]+= ( cos(cosines[1]) ) * older[2];
return;
}
```

```

/*****
MODULE      :      BROADEN.CPP
PURPOSE      :      The BROADEN module contains a single function,
                        convolute(), designed to convolute the calculated
                        line shape with either a Gaussian or Lorentzian line
                        broadening function or some mixture of the two.
                        The convolution is controlled by the parameters
                        _fGB, _fLB, and _fGBLB.
DATE          :      February, 1994
PROGRAMMER:      Klaus Eichele
*****/

```

```
#include "powder.h"
```

```

/* -----
                        FUNCTION CONVOLUTE()

```

Convolutes the spectrum with a Gausso-Lorentzian line shape. Line broadening employs normalized peaks to preserve relative areas independent of line broadening parameters.

```

                        fXG   =   computed line broadening factor Gaussian
                        fXL   =   computed line broadening factor Lorentzian

```

```
-----*/
```

```

int Convolute(float *Spec, int Points, float _fInc)
{
    long i, j, m, n;
    float fXG, fXL, fBF1, fBF2, fNorm, fHeight;
    float fInten, fRj, fImin;
    float *Brod;                // holds broadened spectrum
    float _fGBLB = 0;           // controls Gaussian/Lorentzian mix
    float _fGB   = 400.0;       // Gaussian line broadening factor
    float _fLB   = 0.0;         // Lorentzian line broadening factor

```

```
    printf("Now Broadening the Spectrum ...\n");
```

```

/* -----
                        first need to check and see if line broadening necessary

```

```
-----*/
```

```

if (_fGBLB < 0.0)      _fGBLB = 0.0;
if (_fGBLB > 100.0)    _fGBLB = 100.0;
if (_fGBLB == 0.0)    _fLB = 0.0;        // pure Gaussian
if (_fGBLB == 100.0) _fGB = 0.0;        // pure Lorentzian
// no broadening necessary since smaller than resolution
if ((_fGB < 0.94*_fInc) && (_fLB < 0.64*_fInc)) return (1);

```

```

f1min = 0.00001;                                // threshold

/* -----
                                compute Gaussian factors
-----*/
if (_fGB == 0.0)
{ fBF1 = 0.0; fXG = 0.0; }
else { fBF1 = (100.0 - _fGBLB)/100.0; fXG = -2.7725887/(_fGB*_fGB); }

/* -----
                                compute Lorentzian factors
-----*/
if (_fLB == 0.0)
{ fBF2 = 0.0; fXL = 1.0; }
else { fBF2 = _fGBLB/100.0; fXL = 4.00/(_fLB*_fLB); }

/* -----
                                compute normalization factor
-----*/
fNorm = _fnc/(fBF1*1.064467*_fGB + fBF2*1.5707963*_fLB);

/* -----
                                allocate and zero memory for buffer which holds broadened spectrum
-----*/
Brod = (float *) malloc(Points*(sizeof(float)));
if (Brod == NULL)
{
    printf("Memory Allocation Failed!!\n"
           "Terminating execution!!\n\n");
    sleep(2);
    exit(1);
}
setmem(Brod, Points*sizeof(float), NULL);

/* -----
                                start convolution of the spectrum
-----*/
for (i=0; i<Points; i++)
{
    if (Spec[i] == 0.0) continue;    // nothing there
    fHeight = Spec[i] * fNorm;
    Brod[i] += fHeight;
    j = 1;
    do
    {

```

```

    fRj    = j * _fInc;
    fInten = fBF1 * fHeight * exp(fXG*fRj*fRj) +
             fBF2 * fHeight / (1 + fXL*fRj*fRj);
    m      = i - j;
    n      = i + j;
    if (m >= 0) Brod[m] += fInten;
    if (n < Points) Brod[n] += fInten;
    j++;
    } while (fabs(fInten) >= fImin);
}

/* -----
    reassign convoluted spectrum to *Spec and free memory
-----*/
for (i=0; i<Points; i++) Spec[i] = Brod[i];
free(Brod);
return (0);
}

```

```

/*****
MODULE      :      GRAPH.CPP
PURPOSE     :      The GRAPH module is included in order to view
                    the calculated spectrum on screen after convolution.
                    The code is not "fancy" and no chemical shift axis
                    is displayed. However, it is useful when trying to
                    optimize a fit and more efficient than writing data
                    to a file and reading this into another program after
                    each calculation.

DATE        :      February, 1994
PROGRAMMER:      Klaus Eichele
*****/

```

```
#include "powder.h"
```

```

// global variables
int   GraphDriver;      // the Graphics device driver
int   GraphMode;        // the Graphics mode value
double AspectRatio;     // aspect ratio of a pixel on the screen
int   MaxX, MaxY;       // the maximum resolution of the screen
int   MaxColors;        // the maximum # of colors available
int   ErrorCode;        // reports any graphics errors
struct palettetype palette; // used to read palette info

```

```
void Initialize(void);    // function prototype
```

```

/* -----
                        FUNCTION DISPLAY()

```

Display() is called from within main() after the spectrum has been calculated and convoluted and simply outputs the spectrum to the screen.

```
-----*/
```

```

int Display(struct SpecParam *Simul)
{
int points, Xmax = 600, Ymax = 400, i;
float incx, incy, x, y, *Spec;

```

```

Spec  = Simul->Spectrum;
points = Simul->Points;

```

```

// constants to scale digital resolution and intensity data
// so powder pattern will fill screen
incx  = (Simul->Incr)*Xmax/(Simul->Width);
incy  = ((Simul->Max)-(Simul->Min))/Ymax;

```

```

if (incy == 0.) incy = 1.0;

Initialize();                // set system into graphics mode
setlinestyle(SOLID_LINE, 0, NORM_WIDTH ); // line style of spectrum
setcolor(LIGHTMAGENTA);     // color of spectrum
x = 20;                      // coordinates of starting pixel
y = 410;
moveto(x,y);                // move to this starting pixel

// draw the spectrum
for (i=0; i<points; i++)
{
    x = 20 + i*incx;
    y = 410 - Spec[i]/incy;
    lineto(x,y);
}

getch();                    // pause to view the spectrum
closegraph();               // return the system to text mode
return(0);
}

/* -----
                        FUNCTION INITIALIZE()
-----*/

Sets the system into graphics mode before displaying the spectrum.
-----*/

void Initialize(void)
{
    int xasp, yasp;          // Used to read the aspect ratio

    GraphDriver = DETECT;    // Request auto-detection
    initgraph( &GraphDriver, &GraphMode, "" );
    ErrorCode = graphresult(); // Read result of initialization
    if( ErrorCode != grOk )    // Error occurred during initialization
    {
        printf(" Graphics System Error: %s\n", grapherrormsg( ErrorCode ) );
        exit( 1 );
    }

    getpalette( &palette );  // Read the palette from board
    MaxColors = getmaxcolor() + 1; // Read maximum number of colors
    MaxX = getmaxx();
    MaxY = getmaxy();         // Read size of screen
    getaspectratio( &xasp, &yasp ); // read the hardware aspect

```



```

AspectRatio = (double)xasp/(double)yasp; // Get correction factor
}

```

```

/* -----
                        FUNCTION GETMINMAX()

```

Determines the minimum and maximum intensity within the spectrum array pointed to by *spec. This function is called from within the SETUP module before the function DISPLAY() is called. It is used in scaling the calculated spectrum to full-screen.

```

-----*/
int GetMinMax(float *spec, float *max, float *min, int points)
{
    int i;
    *min  = 0.0;           // value of minimum intensity
    *max  = 0.0;           // value of maximum intensity

    for (i=0; i < points; i++)
    {
        if (spec[i] > *max) *max  = spec[i];
        if (spec[i] < *min) *min  = spec[i];
    }
    return 0;
}

```

```

/*****
MODULE      :      POWDER.CPP
PURPOSE      :      The POWDER module performs the powder
                        averaging. A detailed description of this module is
                        provided below.
*****/
/*      This program module contains the functions Powder and Tent. The module Line
        required by Powder should be passed as a pointer.

```

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REFERENCE: D. W. Alderman, M. S. Solum, D. M. Grant,
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REVISED: Klaus Eichele
 June 9, 1992

TRANSLATED: Translated into C++ language by Klaus Eichele. February 12,
 1994.

DESCRIPTION: POWDER computes the powder sample NMR spectrum which
 results from a single line whose position and amplitude is a
 function of the orientation of each small single crystallite. The user
 specifies the nature of this dependence by supplying a subroutine
 LINE. LINE must then calculate the frequency and amplitude of
 the NMR line corresponding to the direction cosines of the
 magnetic field vector relative to the interaction frame. POWDER
 sums contributions only over a half-sphere on the assumption that
 the sign of the direction of the magnetic field does not alter the
 line position or amplitude. The vertical scale of the spectrum
 produced by POWDER is arbitrary and depends both on the
 number of points in the spectrum and on the parameter NT
 described below. Two spectra produced by two calls to POWDER
 with the same number of points and value of NT have the correct
 relation to one another. POWDER achieves its efficiency by using
 a two dimensional interpolation scheme and by dividing the sphere
 using the symmetry of an octahedron. NT is the number of
 intervals into which the edge of the octahedron is divided to

produce a triangular grid on each face. The total number of frequency-amplitude calculations required is $2*NT*NT + 1$. A value of 32 is typical of this parameter. The calculation may be done faster at the expense of accuracy by decreasing NT. While the lower limit of NT equals 1, the upper limit is determined by the memory requirements of the arrays `FREQ(NT,2*NT)` and `AMP(NT,2*NT)`.

```

*/

#include "powder.h"

#define NNTT 32
/* -----
                                FUNCTION POWDER()

                                Powder has the following return values:
                                0  =  ok
                                1  =  Not enough memory available
                                2  =  Some sort of division by zero attempted
                                3  =  Single-line subspectrum
                                4  =  contributions outside spectrum
                                -----*/

int Powder(struct SpecParam *Simul, int (*Line)( float cosx,
                                                float cosy,
                                                float cosz,
                                                float *freq,
                                                float *amp,
                                                struct SpecParam *Simul)
        )

{
/* ----- Declarations ----- */
int i, j, nt, check;
float x, y, z, r, *freqp, *ampp;
float freq1, freq2, freq3, amp1, amp2, amp3;
float *freq, *amp;

/* -----
                                start by getting the arrays for storage of FREQ and AMP
                                -----*/

nt = Simul->NT;
freq = (float *) malloc((nt+1)*(2*nt+1) * sizeof(float));
if (freq == NULL) return 1;
amp = (float *) malloc((nt+1)*(2*nt+1) * sizeof(float));

```

```
if (amp == NULL) return 1;
```

```
/* -----
PARTITION:      Compute frequencies and amplitudes at triangular grid
                  intersections on faces of octahedron
-----*/
```

```
for (j = 0; j < nt; j++)
{
    /*      this computes frequencies and amplitudes at the inter-
              sections of the octahedron face in the (+x,+y,+z)
              octant, except for z = nt (== top)      */

    for (i = 0; i <= nt-j; i++)
    {
        x = nt - i - j;
        y = i;
        z = j;
        r = sqrt(x*x + y*y + z*z);
        freqp = ((freq+i*(2*nt+1))+j);
        ampp = ((amp +i*(2*nt+1))+j);
        check = Line(x/r, y/r, z/r, freqp, ampp, Simul);
        if (check) return check;
        *ampp = (*ampp)/r/r/r;
    }

    /*      this computes frequencies and amplitudes at the inter-
              sections of the octahedron face in the (-x,+y,+z)
              octant, except for x = 0 (== edge), for y = 0 (== edge),
              and for z = nt (== top)      */

    for (i = nt-j+1; i <= nt; i++)
    {
        x = nt - i - j;
        y = nt - j;
        z = nt - i;
        r = sqrt(x*x + y*y + z*z);
        freqp = (freq+i*(2*nt+1))+j;
        ampp = (amp +i*(2*nt+1))+j;
        check = Line(x/r, y/r, z/r, freqp, ampp, Simul);
        if (check) return check;
        *ampp = (*ampp)/r/r/r;
    }
}
```

```
for (j = nt; j < 2*nt; j++)
{
    /*      this computes frequencies and amplitudes at the inter-
              sections of the octahedron face in the (-x,-y,+z)
```

```

    octant, except for y = 0 (== edge), for z = 0 (== bottom)
    and for z = nt (== top)    */

for (i = j-nt+1; i < nt; i++)
{
    x = -nt - i + j;
    y = nt - j;
    z = nt - i;
    r = sqrt(x*x + y*y + z*z);
    freqp = (freq+i*(2*nt+1))+j;
    ampp = (amp +i*(2*nt+1))+j;
    check = Line(x/r, y/r, z/r, freqp, ampp, Simul);
    if (check) return check;

    *ampp = (*ampp)/r/r/r;
}

/*    this computes frequencies and amplitudes at the inter-
    sections of the octahedron face in the (+x,-y,+z)
    octant, except for y = 0 (== edge), for z = 0 (== bottom)
    and for z = nt (== top)    */

for (i = 1; i <= j-nt; i++)
{
    x = -nt - i + j;
    y = -i;
    z = 2*nt - j;
    r = sqrt(x*x + y*y + z*z);
    freqp = (freq+i*(2*nt+1))+j;
    ampp = (amp +i*(2*nt+1))+j;
    check = Line(x/r, y/r, z/r, freqp, ampp, Simul);
    if (check) return check;
    *ampp = (*ampp)/r/r/r;
}

}

/*    this computes the frequency and amplitude for the top of the
    octahedron, (0,0,nt).    */
freqp = (freq+0*(2*nt+1))+nt;
ampp = (amp +0*(2*nt+1))+nt;
check = Line(0., 0., 1., freqp, ampp, Simul);
if (check) return check;
*ampp = (*ampp)/nt/nt/nt;

/*    this part copies the data of the bottom line of the (+x,+y,+z)
    octant to the bottom line, (-x,-y,0), of the (-x,-y,+z) octant,

```

```

        since they are related by inversion */
for (i = 0; i <= nt; i++)
{
    *((freq+nt*(2*nt+1))+nt+i) = *((freq+i*(2*nt+1))+0);
    *((amp +nt*(2*nt+1))+nt+i) = *((amp +i*(2*nt+1))+0);
}

/*      this part copies the data of the bottom line of the (-x,+y,+z)
        octant to the bottom line, (+x,-y,0), of the (+x,-y,+z) octant,
        since they are related by inversion, except for x = 0 (== edge)
        and for y = 0 (== edge) */
for (j = 1; j < nt; j++)
{
    *((freq+(nt-j)*(2*nt+1))+2*nt) = *((freq+nt*(2*nt+1))+j);
    *((amp+ (nt-j)*(2*nt+1))+2*nt) = *((amp +nt*(2*nt+1))+j);
}

/* -----
INTERPOLATION: Form a spectrum from frequencies and intensities at the
                triangular grid intersections on the faces of the octahedron
                by adding "tents" to the spectrum
-----*/
for (i = 0; i < nt; i++)
{
    for (j = 0; j < nt; j++)
    {
        freq1 = *((freq+(i+1)*(2*nt+1))+j);
        amp1  = *((amp +(i+1)*(2*nt+1))+j);

        freq2 = *((freq+i*(2*nt+1))+j+1);
        amp2  = *((amp +i*(2*nt+1))+j+1);

        freq3 = *((freq+i*(2*nt+1))+j);
        amp3  = *((amp +i*(2*nt+1))+j);

        check = Tent(freq1, freq2, freq3, amp1+amp2+amp3, Simul);
        if (check == 2 || check == 4) return check;

        freq1 = *((freq+(i+1)*(2*nt+1))+j);
        amp1  = *((amp +(i+1)*(2*nt+1))+j);

        freq2 = *((freq+i*(2*nt+1))+j+1);
        amp2  = *((amp +i*(2*nt+1))+j+1);

        freq3 = *((freq+(i+1)*(2*nt+1))+j+1);
        amp3  = *((amp +(i+1)*(2*nt+1))+j+1);

        check = Tent(freq1, freq2, freq3, amp1+amp2+amp3, Simul);

```

```

        if (check == 2 || check == 4) return check;
    }
    if (i)
    {
        for (j = nt; j < 2*nt; j++)
        {
            freq1 = *((freq+i*(2*nt+1))+j);
            amp1   = *((amp +i*(2*nt+1))+j);

            freq2 = *((freq+(i+1)*(2*nt+1))+j+1);
            amp2   = *((amp +(i+1)*(2*nt+1))+j+1);

            freq3 = *((freq+(i+1)*(2*nt+1))+j);
            amp3   = *((amp +(i+1)*(2*nt+1))+j);

            check = Tent(freq1, freq2, freq3, amp1+amp2+amp3, Simul);
            if (check == 2 || check == 4) return check;

            freq1 = *((freq+i*(2*nt+1))+j);
            amp1   = *((amp +i*(2*nt+1))+j);

            freq2 = *((freq+(i+1)*(2*nt+1))+j+1);
            amp2   = *((amp +(i+1)*(2*nt+1))+j+1);

            freq3 = *((freq+i*(2*nt+1))+j+1);
            amp3   = *((amp +i*(2*nt+1))+j+1);

            check = Tent(freq1, freq2, freq3, amp1+amp2+amp3, Simul);
            if (check == 2 || check == 4) return check;
        }
    }
}

/* -----
                                POWDER finished release memory
-----*/
free(freq);
free(amp);
return 0;
}

/* -----
                                FUNCTION TENT()

```

Tent is called by Powder. It adds a "tent" to the spectrum which represents the contribution from a triangle on the vertices of which the frequencies are *freq1*, *freq2*, and

freq3. First, the frequencies are sorted according to magnitude, and the spectrum indices are computed. The cases mentioned below refer to the equations given in the paper by Alderman, Solum, and Grant.

```

-----*/
/*      This part has been modified by Klaus Eichele, November 1992, to meet the
common uses in NMR, i.e., the address of a spectrum array bin is increasing
with decreasing frequency. For this purpose, the definitions of fmax, fmid, and
fmin as highest, intermediate, and lowest frequencies of the triangle have been
retained, as well as the definitions of f1 and f2 as low and high frequency limits
of the spectrum bin. However, the order of the case selections has been
completely reversed to conform with the reversed addresses.
*/

/*      Tent has the following return values:      0 = everything ok
                                                    2 = some sort of division by zero
                                                    3 = single-line subspectrum
                                                    4 = contributions outside spectrum
*/

int Tent(      float freq1, float freq2, float freq3, float amp,
               struct SpecParam *Simul      )
{
    int points, retu, np, npmid, npmax, j, i;
    float fmin, fmid, fmax, f1, f2, top, *spec, buffer[3], finc;
    float higf, lowf;

    /* -----
                                assign some parameters
    -----*/

    retu    = 0;
    points  = Simul->Points;
    finc    = Simul->Incr;
    higf    = Simul->HiFreq;
    spec    = Simul->Spectrum;
    if (points < 4 || finc == 0.) return 2;

    /* -----
                                sort frequencies
    -----*/

    buffer[0] = freq1; buffer[1] = freq2; buffer[2] = freq3;
    for (i = 0; i < 3; i++)
    {
        float temp;
        for (j = 0; j <= 2-i; j++)

```



```

        {      if (buffer[j] > buffer[j+1])
                {      temp = buffer[j]; buffer[j] = buffer[j+1];
                        buffer[j+1] = temp;
                }
        }
}
fmin = buffer[0]; fmid = buffer[1]; fmax = buffer[2];

/* -----
                        compute height of tent
-----*/
/*      Note: if the total subspectrum arises from a single line, fmax = fmin, and
causes trouble in this step since there is no area defined for a single line!
In this case, fmax-fmin is set to the digital resolution to get around this
problem. It is not a great solution but usually does the trick. Set a marker
to report the occurrence of this problem.
*/
if (fmax == fmin)
{      top = amp/finc;
    retu = 3;          // marker for single line
}
else top = amp / (fmax - fmin);

/* -----
                        compute indices of tent edges and top
-----*/
np      = (higf-fmax)/finc;
npmid   = (higf-fmid)/finc;
npmax   = (higf-fmin)/finc;

/* -----
                        look for contributions outside the spectrum
-----*/
if ((npmax >= points) || (np < 0)) return 4;

/* -----
                        erect "tent" by examining various cases
-----*/
// case 1g(2) & 1a(2)
// in this case, the bin contains both NP and NPMID.
if (np == npmid) spec[np] = spec[np] + (fmax-fmid)*top;
else
{      // case 1i
        // in this case, only the corner containing NP lies in the bin.

```

```

f1 = higf - finc*(np+1);
spec[np] = spec[np] + (fmax-f1)*(fmax-f1)*top/(fmax-fmid);
while (np++, f2 = f1, np < npmid)
{
    // case 1h
    // in this case, both NP and NPMID lie outside the bin;
    // NP is incremented until NPMID lies in the bin as well.
    f1 = higf - finc*(np+1);
    spec[np] = spec[np] + finc*((fmax-f1)+(fmax-f2))*top/(fmax-fmid);
}

// case 1e(2) & 1f(2)
// now the middle of the triangle is within the bin.
spec[np] = spec[np] + (f2-fmid)*((fmax-f2)+(fmax-fmid))*top/(fmax-fmid);
}

// case 1e(1) & 1a(1)
// in this case, both NP and NPMAX lie within the bin.
if (np == npr.ax) spec[np] = spec[np] + (fmid-fmin)*top;
else
{
    // case 1f(1) & 1g(1)
    // in this case, only the center of the triangle lies within the bin.
    f1 = higf-finc*(npmid+1);
    spec[np] = spec[np] + (fmid-f1)*((fmid-fmin)+(f1-fmin))*top/(fmid-fmin);
    while (np++, f2 = f1, np < npmax)
    {
        // case 1d
        // in this case, both NP and NPMAX lie outside the bin;
        // NP is incremented until NPMAX is encountered.
        f1 = higf-finc*(np+1);
        spec[np] = spec[np] + finc*((f2-fmin)+(f1-fmin))*top/(fmid-fmin);
    }

    // case 1c
    // in this case, only the corner with NPMAX lies within the bin.
    spec[np] = spec[np] + (f2-fmin)*(f2-fmin)*top/(fmid-fmin);
}

// the cases 1b and 1j are trivial and are taken care of
// by clearing the spectrum table, i.e. Spec[i] = 0
180: return retu;
}

```

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