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Nuclear Magnetic Resonance Studies of Homonuclear

Spin Systems in Solids

by

Gang Wu

Submitted in partial fulfilment of the requirements

for the degree of Doctor of Philosophy

at

Dalhousie University

Halifax, Nova Scotia

June, 1994

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Abstract

Nuclear magnetic resonance (NMR) spectroscopy of solids has become widely used in the study of a great variety of solid materials. However, new observations are still emerging and many spectral properties are not well-understood, even for simple spin-pair systems consisting of two homonuclear spin-1/2 nuclei. This thesis represents a detailed investigation of NMR spectra arising from homonuclear two-spin systems in both static and rotating solids. The great potential of the dipolar-chemical shift NMR method in characterizing chemical shift tensors is demonstrated for static solids. Using this method, chemical shift tensors involving ¹³C, ¹⁵N and ³¹P nuclei have been determined in various classes of compounds of chemical interest. Some of the compounds investigated exhibit NMR spectra with interesting features which had not been reported previously. It is found that the observed anomalous features could be interpreted as arising from second-order (AB) effects. Based on average Hamiltonian theory, a uniform treatment is developed for interpreting various new observations concerning spinning-frequency dependent phenomena observed in magic-angle-spinning (MAS) NMR spectra of rotating solids. Under slow MAS conditions, factors that determine the resolution limit in MAS NMR spectra arising from two dipolar-coupled spins are studied and the relationships between crystallographic equivalence and MAS NMR spectra are also investigated. Two new applications of variable-angle-spinning (VAS) NMR experiments are demonstrated. It is found that spinning a sample rapidly about an axis other than the magic angle provides a new method for reintroducing Jcoupling between two crystallographically equivalent but magnetically non-equivalent spins. A particular significance of the VAS method is that it yields information concerning the relative orientation between the chemical shift tensors of two J-coupled spins. The VAS method will be useful to systems where the dipolar-chemical shift NMR method is not applicable.

List of Symbols, Abbreviations and Compounds

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Symbols

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$\alpha^{\rm c}, \beta^{\rm c}, \gamma^{\rm c}$	Euler angles defining transformation from crystal-axis-system to rotor-
	axis-system
$\alpha^{cs}, \beta^{cs}, \gamma^{cs}$	Euler angles defining chemical shift tensor in dipolar tensor frame
$\alpha^{\mathrm{R}}, \beta^{\mathrm{R}}$	angles defining sample rotation axis in chemical shielding tensor frame
B ₀	applied magnetic field vector
$\mathbf{B}_0 = B_0 $	applied magnetic field strength
D	mixing term
$D_{+\infty}$	rapid spinning limit of mixing term
$\delta_{ m iso}$	isotropic chemical shift
$\delta_{11},\delta_{22},\delta_{33}$	principal components of chemical shift tensors
$\Delta J = J_{\parallel} - J_{\perp}$	anisotropy in J tensor
ϕ_{ii}	angle between dipolar vector and δ_{ii}
γ	magnetogyric ratio
H	spin Hamiltonian
$h=2\pi\hbar$	Planck constant
I	dimensionless nuclear spin angular momentum operator
к	skew of chemical shift tensor
μ	nuclear magnetic dipole moment vector
Ω	span of chemical shift tensor
$\omega_0 = 2\pi\nu_0$	Larmor frequency

$\omega_R/2\pi$	sample spinning frequency in Hz
$\omega_R^{scaled}/2\pi$	scaled sample spinning frequency in Hz
$\omega_J/2\pi = J_{iso}$	isotropic indirect spin-spin coupling constant in Hz
$\omega_{\Delta}/2\pi$	isotropic chemical shift difference in Hz
r	internuclear (dipolar) vector
r	internuclear separation
R	unitary transformation
R _{DD}	dipolar coupling constant
R _{eff}	effective dipolar coupling constant
r_{XX}, r_{YY}, r_{ZZ}	dipolar tensor frame
$\sigma_{ m iso}$	isotropic chemical shielding constant
$\sigma_{11}, \sigma_{22}, \sigma_{33}$	principal component of chemical shielding tensor
σ _d	diamagnetic contribution to chemical shielding
$\sigma_{\rm p}$	paramagnetic contribution to chemical shielding
$ heta,\phi$	angles defining dipolar vector in laboratory frame
θ_C, ϕ_C	angles defining dipolar vector in crystal-axis-system
$ heta_D, \phi_D$	angles defining applied magnetic field in dipolar tensor frame
θ_R	angle between dipolar vector and sample spinning axis
θ_{S}	sample spinning angle
Т	effective dipolar-chemical shift tensor
T_1, T_2, T_3	principal component of effective dipolar-chemical shift tensor
T_R	rotor period

n

Abbreviations

AHT	average Hamiltonian theory
CAS	crystal-axis-system
СР	cross polarization
LAB	laboratory frame
MAS	magic-angle spinning
NMR	nuclear magnetic resonance
ppm	parts per million
RAS	rotor-axis-system
RF	radiofrequency
RR	rotational resonance
VAS	variable-angle spinning

Compounds

- 1 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide
- 2,4-bis(methylthio)-1,3-dithia-2,4-diphosphetane-2,4-disulfide
- 3 *trans*-stilbene- α , β -¹³C₂
- 4 bis(triphenylphosphine)(*trans*-stilbene- α , β -¹³C₂)platinum(0)
- 5 tetraethyldiphosphine disulfide
- 6 *cis*-2,10-dimethyl[1,2,3]benzothiadiphospholo[2,3b]benzothiaphosphole
- 7 phenylacetic acid-1,2- $^{13}C_2$
- 8 potassium phenylacetate- $1,2^{-13}C_2$

9 cis-azobenzene-¹⁵N₂

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- 10 cis-azobenzene-¹⁵N₂ dioxide
- 11 *trans*-1-phenyl-2-methyl-3,4-bis(*tert*-butyl)diphosphete
- 12 *cis*-1-phenyl-2-methyl-3,4-bis(*tert*-butyl)diphosphete
- 13 bis(methyldiphenylphosphine)(1,5-cyclooctadiene)iridium(I) hexafluorophosphate
- 14 *cis*-dichlorobis(triethylphosphine)platinum(II)
- 15 bis(triphenylphosphine)mercury(II) nitrate
- 16 tetrakis-(2-phenyl-3,4-dimethylphosphole-1,5-diyl)
- 17 *cis*-1,2-(diphenylphosphino)ethylene

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Chapter 1

Introduction

The nuclear magnetic resonance (NMR) phenomenon was first discovered by I. I. Rabi and his co-workers in molecular-beam experiments in the late 1930s (1). However, for nearly a decade, NMR was appreciated only by a handful of nuclear physicists. This situation was dramatically changed after NMR was discovered in bulk matter in 1946 independently by Purcell, Torrey, and Pound (2), and by Bloch, Hansen, and Packard (3). Since then, NMR spectroscopy has become an entirely new science widely applied in a variety of disciplines such as chemistry, biology and medicine, to name just a few.

Interestingly, at the beginning of NMR spectroscopy, the difference between NMR in liquids and in solids was not apparent. In fact, Purcell *et al.* discovered NMR in *solid* paraffin (2) whereas Bloch *et al.* discovered it in *liquid* water (3). However, when weaker interactions such as chemical shielding (4) and J interactions (5,6) were discovered in liquids, NMR spectroscopy turned out to be an extremely useful technique for chemists to characterize chemical systems in the liquid state. Unfortunately, NMR spectra of solids generally consist of peaks that are so broad that these weak interactions are obscured. Therefore, NMR spectroscopy in solids became less popular than in liquids.

Over the more than twenty years when solution state NMR spectroscopy enjoyed an overwhelming success and became the most important analytical technique for

chemists. NMR spectroscopy in solids gradually developed itself more-or-less in the Several important experiments are worth mentioning. In the late 1950s, shadow. And rew et al. (7) and Lowe (8) independently discovered that, by rapidly rotating a solid sample about a direction inclined 54°44' from the external magnetic field, strong direct dipole-dipole interactions can be eliminated. This technique is now well-known as magic-angle spinning (MAS). However, at the time when MAS was first demonstrated, the technical difficulties involved precluded its useful application to systems of chemical interest and the effectiveness of the method remained unappreciated for almost twenty years. In 1962, Hartmann and Hahn (9) demonstrated a double-resonance method to study magnetically dilute spins in solids. They showed that, by setting up a thermal contact between an abundant and a dilute spin system, magnetically dilute spins can be studied *indirectly* by observing their accumulative effects on the abundant spin system. Although this indirect method showed a great promise in improving sensitivity, it suffered greatly from poor resolution. A significant breakthrough was made by Pines, Gibby and Waugh in 1972 (10). They introduced a *direct* method to observe NMR signals of magnetically dilute spins. The advantage of their method is that significant gains in both sensitivity and resolution are realized. Basically, they used a cross polarization (CP) technique, which was adopted from the double-resonance concept of Hartmann and Hahn (9), to enhance NMR signals of dilute spins and applied an abundant spin CW decoupling technique during data acquisition in order to improve resolution. Their experiments were so successful that chemical shielding anisotropy of low abundant nuclei such as ¹³C, ²⁹Si and ¹⁵N could readily be measured in polycrystalline samples

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(10-13). In such NMR experiments the spectral broadening arising from heteronuclear dipolar interactions among the abundant and dilute spins can be removed and the resolution is controlled only by chemical shielding anisotropy. However, for magnetically dilute spins, chemical shielding anisotropy is often very large and, furthermore, even for a small molecule containing only few carbons, overlapping anisotropic shielding powder patterns could result in a poorly-resolved spectrum. NMR spectroscopy of solids remained just one step outside of the realm of a high-resolution spectroscopic technique until the work of Schaefer and Stejskal in 1976 (14). They simply demonstrated that, for rigid solids, a combination of the old technique of MAS and the techniques of CP and high-power spin decoupling can produce NMR spectra consisting of narrow peaks similar to solution state NMR spectra. Since then, CP/MAS NMR has become an increasingly popular acronym which simply means high-resolution NMR spectroscopy in solids.

Since the stage was set, NMR spectroscopy of solids has experienced a dramatic growth, particularly in the last decade. Today, it is generally accepted that NMR spectroscopy of solids is feasible for studies of a great variety of chemical systems and is an invaluable method bridging solution state NMR and diffraction techniques. This rapid expansion in chemical applications of solid state NMR spectroscopy has been brought about for several reasons. First, the great improvement of commercial NMR spectrometers in the past ten years has made solid state NMR experiments routine. Second, there is potentially more information in solid state NMR spectra. Third, NMR parameters such as the chemical shift and the dipolar coupling constant are influenced

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only by the short-range environment around the nucleus of interest. Therefore, NMR is amenable to studies of che.nical systems such as semi-crystalline and amorphous polymers that cannot be obtained in crystalline form, making various diffraction techniques difficult to apply. Finally, a large number of chemical systems such as cross-linked polymers and ceramics are insoluble in common solvents and hence are not suitable for solution state NMR study.

This thesis is concerned with NMR studies of homonuclear spin systems in solid polycrystalline powdered samples. One of the primary objectives is to illustrate how one can use the homonuclear dipolar interaction to obtain information about the orientation of chemical shielding tensors from NMR spectra of static solids. Another main objective is to demonstrate how one can extract new information about the J coupling constant between equivalent spins, the crystallographic equivalence and the orientation of chemical shielding tensors from NMR spectra of *rotating* solids. In particular, attention will be focused on investigations of solid-state NMR spectra arising from isolated homonuclear spin pairs that consist of magnetically dilute spin-1/2 nuclei including ¹³C, ¹⁵N and ³¹P. The remainder of this thesis will be organized as follows. In Chapter 2, a general theoretical background necessary to appreciate the information available from solid state NMR spectra will be presented. Each of the nuclear spin interactions important for spin-1/2 nuclei will be outlined. Also, basic techniques used in carrying out a solid state NMR experiment will be described. In Chapter 3, a detailed study of NMR spectra arising from homonuclear two-spin systems in static solids will be given. The determination of chemical shift tensors of ¹³C, ¹⁵N and ³¹P nuclei in various chemically important

compounds will be presented. Chapter 4 will describe a uniform treatment of MAS NMR spectra arising from homonuclear two-spin systems. Recent new experimental observations concerning the spinning-frequency dependence of MAS NMR spectra will be interpreted using the derived theoretical expressions. In Chapter 5, new applications of variable-angle-spinning (VAS) NMR experiments for rotating solids will be demonstrated. Finally, a brief summary and possible extensions of the work outlined in this thesis will be given in Chapter 6.

Chapter 2

Nuclear Magnetic Resonance Spectroscopy of Solids

NMR spectroscopy, like all other spectroscopic techniques, involves the study of a particular set of energy levels *via* the interaction between electromagnetic radiation and matter. More precisely, NMR spectroscopy deals with energy levels involving nuclear spins in the presence of a strong, static magnetic field. The electromagnetic radiation employed in NMR lies in the range of radiofrequency (RF), thus NMR spectroscopy is sometimes termed as radiofrequency spectroscopy.

Generally one can treat the nuclear spin system as an isolated system. That is, it is only necessary to consider a reduced spin Hamiltonian rather than a total Hamiltonian of the entire molecular system. Interactions of the nuclear spin system under observation with all other degrees of freedom including all possible time-dependent random interactions between the nuclear spins and environment are ascribed to the "lattice". Interactions between nuclear spins and the lattice are important in understanding various relaxation phenomena, but this thesis is not concerned with NMR relaxation phenomena.

2.1 Nuclear spin interactions in solids

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For nuclear spin systems containing only spin-1/2 nuclei, the following four nuclear spin interactions have to be considered for diamagnetic solids: (i) the Zeeman interaction, (ii) the chemical shielding interaction, (iii) the direct magnetic dipole-dipole

interaction, and (iv) the indirect electron-mediated spin-spin interaction or the J interaction.

2.1.1 The nuclear Zeeman interaction

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The basic as well as the strongest interaction in NMR is the interaction between a nuclear magnetic dipole moment, μ , and an external magnetic field, B_0 , namely the nuclear Zeeman interaction. A nuclear magnetic dipole moment is the intrinsic property of a nucleus and is related to the total nuclear spin angular momentum, $\hbar l$, by the following equation:

$$\mu = \gamma \hbar I \tag{2.1}$$

where γ is the magnetogyric ratio and $\hbar = h/2\pi$ (*h* is Planck's constant). The magnitude of the nuclear spin angular momentum is given by $\hbar[I(I+1)]^{1/2}$, where I is either an integer or half-integer. If the direction of the external magnetic field is defined as the *z* direction, the nuclear Zeeman Hamiltonian can be written as

$$\mathcal{H}_{z} = -\mu \cdot B_{0} = -\gamma \hbar I \cdot B_{0} = -\gamma \hbar |B_{0}| m_{z} \qquad (2.2)$$

where m_z is the z-component of the nuclear spin angular momentum ($m_z = I, I-1, ..., -I$). For a nucleus with $I = \frac{1}{2}$, m_z takes values of $+\frac{1}{2}$ and $-\frac{1}{2}$, leading to a two-level system (Fig.2.1). The two spin states are usually denoted as $|\alpha \rangle$ ($m_z = +\frac{1}{2}$) and $|\beta \rangle$ ($m_z = -\frac{1}{2}$), or as the "up" and "down" spin states, respectively. The energy separation between the two nuclear spin states is given by: ۱

$$\Delta E = \gamma \hbar |B_0| \tag{2.3}$$

In the presence of electromagnetic radiations, transitions between the two nuclear spin states may be induced if the quanta of applied radiation satisfy the following condition:

$$\hbar\omega_0 = h\nu_0 = \gamma\hbar |B_0| \tag{2.4}$$

where ω_0 or ν_0 is known as the Larmor frequency in units of rad \cdot s⁻¹ or s⁻¹, respectively. The magnitude of the nuclear Zeeman interaction is usually expressed by the Larmor frequency. It is clear from Eq.(2.4) that the nuclear Zeeman interaction depends on the



Figure 2.1 Energy level diagram of a spin-¹/₂ nucleus in the presence of an external magnetic field.

magnetogyric ratio of the nuclear species under observation and the strength of the applied magnetic field, B_0 . For protons, typical nuclear Zeeman interactions in the magnetic field of modern NMR spectrometers ($B_0 = 2.35-17.62$ T) are in the range of

100-750 MHz. The nuclear Zeeman interaction is extremely weak compared with interactions studied by other spectroscopic techniques. For example, the nuclear Zeeman interaction energy of protons in a magnetic field of 14.10 T corresponds to a thermal energy of 28.8 mK.

In a macroscopic sample, one deals with a large number of nuclear spins (10¹⁸ - 10²³). At thermal equilibrium the population of nuclear spins in $|\alpha\rangle$ and $|\beta\rangle$ states is given by the Boltzmann distribution:

$$\frac{n_{\beta}}{n_{\alpha}} = \exp(-\Delta E/kT) = \exp(-\gamma \hbar |B_0|/kT)$$
(2.5)

Since the nuclear Zeeman interaction is extremely weak, it results in an extremely small population difference between $|\alpha\rangle$ and $|\beta\rangle$ states. For instance, $n_{\beta}/n_{\alpha} = 0.99996$ for ¹H at 300 K in a magnetic field of 14.10 T. This fact makes NMR spectroscopy a rather *insensitive* spectroscopic technique in a sense that a relatively large number of nuclear spins are required in order to make NMR signals detectable. However, the extremely weak nuclear spin interactions make it possible for atomic nuclei to become a microscopic probe extremely sensitive to subtle variations in molecular and electronic structures.

It is clear from Eq.(2.2) that the nuclear Zeeman interaction is of no explicit interest for chemists, since all nuclei of a given isotope would absorb RF radiations at the same frequency. If the nuclear Zeeman interaction were the only nuclear spin interaction present, NMR would have no use to chemists. However, the nuclear Zeeman interaction is analogous to the carrier wave in radio broadcasting, without which all beautiful "music" arising from other subtle nuclear spin interactions could not be enjoyed.

2.1.2 The chemical shielding interaction

In the above discussion of nuclear Zeeman interactions, one in fact deals with a bare nucleus; however, chemists are most interested in molecules. This implies that one must consider nuclei surrounded by electrons. Therefore, interactions among nuclei, electrons and an external magnetic field become important. It is well-known that electron circulating motions induced by an external magnetic field will generate a secondary magnetic field at the nucleus. Thus, a nucleus will generally experience a magnetic field which is slightly different from the applied one. This phenomenon is known as chemical shielding. The effective magnetic field at the nucleus can be written as:

$$B_{eff} = (1 - \sigma) B_0$$
 (2.6)

where σ is a small, dimensionless quantity ($\sigma \ll 1$) and is called the chemical shielding constant. In general, the chemical shielding constant for a particular nucleus in a molecule may be written as a sum of two contributions:

$$\sigma = \sigma_d + \sigma_p \tag{2.7}$$

where σ_d and σ_p are known as the diamagnetic and paramagnetic contribution to a total chemical shielding, respectively. The diamagnetic and paramagnetic contributions to the total chemical shielding can be understood as due to two different types of induced electron circulation. While one type of induced electron circulation produces an additional magnetic field at the nucleus with the direction being anti-parallel to the external field ($\sigma_d > 0$), the other has a magnetic field parallel to B_0 ($\sigma_p < 0$). In the discussion which follows, an attempt will be made to propose a simple picture for understanding the two different types of electron circulation that lead to diamagnetic and paramagnetic shielding contributions, respectively. Although a full quantum-mechanical treatment of chemical shielding has been available for many years (15), a simple picture based on classical physics for visualizing the paramagnetic contribution is rarely found in any textbooks.

Diamagnetic circulation. Electrons orbiting around the central nucleus can be visualized as moving charged particles, hence, they are subject to a Lorentz force when placed in a magnetic field. As is known from classical electromagnetism, the effect of a Lorentz force is to cause all electrons to rotate about the magnetic field. The consequence of such an electron rotation is *equivalent* to an electric current, which in turn produces an additional magnetic field at the nucleus with the direction being antiparallel to the external magnetic field. Therefore, the nucleus feels a slightly weaker magnetic field than the actual applied magnetic field. In other words, the nucleus is shielded by the surrounding electrons. This is known as the diamagnetic contribution to the total chemical shielding. The apparent current (due to the motion of all electrons) induced by the Lorentz force is sometimes termed as a diamagnetic current. This is the common picture available for understanding a diamagnetic circulation (*16*).

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Paramagnetic circulation. Clearly, the motion of electrons around the nucleus possesses another property, *i.e.*, orbital angular momentum. Since it is the magnetic

moment associated with an electron orbital angular momentum that interacts directly with the magnetic field, both electron orbital angular momentum and its associated magnetic moment will be used in the discussion that follows. The electron orbital angular momentum property and hence the magnetic moment can be visualized as a property possessed by the *whole* electron cloud. The classical analog of this type of motion would be a loop current, in contrast to the idea that electrons are moving charged particles used when discussing the diamagnetic circulation. It is known in classical physics that a loop current possesses a magnetic moment. Clearly, the idea of loop current is associated with the concept that the electron motion is wave-like. This argument becomes familiar when considering the dual nature of electrons. Therefore, the electron cloud can be thought of as consisting of many loop currents. For example, an electron in a p_x orbital can be treated as a sum of many electric current loops as portrayed in Fig.2.2. All planes of loop currents are parallel to the x axis. Usually a molecule does not possess a permanent magnetic moment, because the loop current always appears in pairs with the



Figure 2.2 A schematic diagram of the loop-current description for a p_x electron.

two current directions being opposite to each other. This is termed as quenching of orbital angular momentum in quantum mechanics (17). The pairing of the loop currents is completely analogous to opposite components of the orbital angular momentum such as $L_z = +1$ and $L_z = -1$. As is well-known in classical physics, the magnetic moment associated with a loop current is perpendicular to the plane of the loop current with the direction being *anti-parallel* to the electron angular momentum. Therefore, the total magnetic moment of an electron cloud also vanishes in the absence of an external magnetic field.

The presence of a strong magnetic field would polarize the loop current pair, that is, it would favour the loop current with the magnetic moment being parallel to it. Therefore, a net magnetic moment results. This magnetic moment or the associated loop current pair will precess about the external magnetic field. It can be shown that all loop current pairs will precess in the same direction. This implies that all electrons that possess orbital angular momentum will have a tendency to precess in the direction of μ $\times B_0$. As an example, a loop current pair is shown Fig.2.3b. It is apparent that the precession direction of the loop currents (that are made of electrons) is opposite to that of electrons in the diamagnetic current. In a molecule, the ease for such a rotation of the whole electron cloud will certainly depend on the position of neighbouring positively charged nuclei. This is the origin of the paramagnetic shielding contribution to the total chemical shielding. From the above discussion, it is clear that the paramagnetic contribution to chemical shielding has its origin from the Zeeman interaction between electron orbital magnetic moments and the external magnetic field. In fact, this is



Figure 2.3 A schematic diagram of diamagnetic (a) and paramagnetic (b) circulations induced by the presence of a strong external magnetic field.

completely analogous to the perturbation Hamiltonian in Ramsey's theory (15). For any molecular direction along which the electronic environment is cylindrically symmetric, the paramagnetic contribution vanishes. This is because in this direction all the loop current planes are parallel to the external field and have zero interaction energy with the external magnetic filed, *i.e.*, $E = -\mu \cdot B_0 = 0$. In this case the electron circulation that originates from an orbital angular momentum will not occur. Of course, diamagnetic currents still contribute to the chemical shielding. In quantum mechanical language, the presence of a strong external magnetic field differentiates different components of the electron angular momentum, leading to an unquenching of the electron orbital angular momentum. The presence of an external field always induces a small unquenched orbital
angular momentum such that the associated unquenched magnetic moment is parallel to the external field.

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It has been shown that the model proposed here, although oversimplified, can be used to understand on the level of classical physics how the two types of electron circulation come into play in the presence of a strong external magnetic field. Three main points are summarized below:

(1) The induced magnetic field by a diamagnetic circulation at the nucleus is antiparallel to the external field, while that by a paramagnetic circulation is parallel to the external field.

(2) A diamagnetic circulation can be understood with the particle nature of electrons whereas a paramagnetic circulation is associated with the orbital angular momentum property of electron motion, which can be seen as a wave property of the *whole* electron cloud.

(3) A diamagnetic circulation can be induced without changing the overall shape or "orientation" of the electron cloud or orbital, whereas the occurrence of a paramagnetic circulation is the result of distorting of the electron cloud or orbital. This point is related to the fact that, in the quantum theory of chemical shielding, the diamagnetic contribution is associated only with the electron ground state whereas the paramagnetic term contains contributions from all excited states. Furthermore, the ease for such a change in the electron cloud orientation is directly related to the energy separation between electron ground and excited states.

It can be readily appreciated that, if the electronic environment at the nucleus

deviates from spherical symmetry, the chemical shielding at the nucleus will depend on the orientation of the molecule with respect to the external magnetic field. In general, the chemical shielding property can be described by a second-rank tensor and the chemical shielding Hamiltonian can be written as:

$$\begin{aligned} \mathfrak{H}_{CS} &= \mu \cdot \sigma \cdot B_{0} = \gamma \hbar \left(I_{x}, I_{y}, I_{z} \right) \cdot \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{xz} & \sigma_{yz} & \sigma_{zz} \end{pmatrix} \cdot \begin{pmatrix} 0 \\ 0 \\ |B_{0}| \end{pmatrix} \\ &= \gamma \hbar (I_{x}, I_{y}, I_{z}) \cdot \begin{pmatrix} \sigma_{xz} \\ \sigma_{yz} \\ \sigma_{zz} \end{pmatrix} |B_{0}| \end{aligned}$$
(2.8)

It is clear from Eq.(2.8) that the chemical shielding introduces an additional magnetic field, $(\sigma_{xz}, \sigma_{yz}, \sigma_{zz})|B_0|$. Since $\sigma \ll 1$, the effective field that a nucleus feels is still approximately along the B_0 direction (*i.e.*, the z direction). This is known as the secular approximation or truncation (18). Under this approximation, the chemical shielding Hamiltonian is rewritten as:

$$\mathcal{H}_{CS} = \gamma \hbar \sigma_{zz} |B_0| I_z \tag{2.9}$$

Usually σ is a general 3 by 3 matrix that can be separated into a symmetric and an antisymmetric matrix; however, the anti-symmetric part does not contribute to σ_{zz} and therefore has no influence on NMR spectra under the secular approximation. The symmetric chemical shielding tensor can always be diagonalized and the three diagonal elements are called principal components of a chemical shielding tensor, denoted as σ_{11} , σ_{22} and σ_{33} ($\sigma_{11} < \sigma_{22} < \sigma_{33}$). The transformation to fulfil such a diagonalization defines the orientation of a chemical shielding tensor with respect to the crystal axis system.

If the direction of the external magnetic field is described by directional cosines $(\cos X_1, \cos Y_2, \cos Z_3)$ in the principal axis system of a chemical shielding tensor, the observed NMR frequency can be written as:

$$\omega = \omega_0 \left[1 - (\sigma_{11} \cos^2 X_1 + \sigma_{22} \cos^2 Y_2 + \sigma_{33} \cos^2 Z_3) \right]$$
(2.10)

Often one has a sample consisting of many small crystallites in the form of a powder. Therefore, the orientation of the crystallites is random with respect to the external magnetic field. This is equivalent to saying that the orientation of the external magnetic field is random in the principal axis system of the chemical shielding tensor for all crystallites. This leads to a distribution of NMR frequencies and the resultant NMR lineshapes are called NMR powder lineshapes or powder patterns. A typical powder pattern due to anisotropic chemical shielding is shown in Fig.2.4.



Figure 2.4 A typical powder pattern due to the anisotropic chemical shielding interaction. The principal components of the chemical shielding tensor are generally expressed in units of parts per million (ppm).

The magnitude of the chemical shielding interaction is much smaller than that of the nuclear Zeeman interaction. However, it is its weakness that makes the chemical shielding interaction the most important NMR interaction for chemists. Atomic nuclei which serve as sensors are spatially localized and are extremely sensitive to the electronic environment around them. For example, in ¹³C NMR spectra of a solid polyethylene sample, it is straightforward to distinguish carbon nuclei that are in crystalline regions from those in amorphous regions (19); the energy difference involved is as small as 0.12×10^{-8} Jmol⁻¹! It is this sensitivity, or perhaps resolution might be a better term, that leads to the many versatile chemical applications of NMR spectroscopy.

It should be mentioned that, in actual NMR experiments, one always measures NMR signals with respect to that of a reference. The difference between NMR signals due to the sample of interest and that of the reference is called the chemical shift, δ , and expressed in units of parts per million (ppm). The relationship between the observed chemical shift and the chemical shielding is given by:

$$\delta_{sample} = 10^6 (\omega_{sample} - \omega_{ref}) / \omega_{ref} \approx \sigma_{ref} - \sigma_{sample}$$
(2.11)

Therefore, a chemical shielding tensor is also related to a chemical shift tensor. Once the absolute shielding for the NMR signal in a reference sample is established, all chemical shift data for the same nuclear species can be easily converted to absolute chemical shieldings. In this thesis, although chemical shielding, σ , will always be used in the equations, chemical shift tensors will be reported in the text.

Although the three principal components of a chemical shift tensor are sufficient to describe the anisotropic chemical shift, three other quantities, known as the isotropic value, the span (Ω) and the skew (κ) of a chemical shift tensor, have recently been suggested to be the standard convention for describing chemical shift tensors (20). Their definitions are given in Eq.(2.12).

$$\sigma_{iso} = \frac{1}{3} \left(\sigma_{11} + \sigma_{22} + \sigma_{33} \right), \ \delta_{iso} = \frac{1}{3} \left(\delta_{11} + \delta_{22} + \delta_{33} \right)$$

$$\Omega = \sigma_{33} - \sigma_{11} = \delta_{11} - \delta_{33} \qquad (2.12)$$

$$\kappa = \frac{3 \left(\sigma_{iso} - \sigma_{22} \right)}{\Omega} = \frac{3(\delta_{22} - \delta_{iso})}{\Omega}$$

The meanings of these three quantities are clear in terms of the appearance of a powder pattern arising from anisotropic chemical shifts. The isotropic value defines the centre of the powder pattern, the span describes the breadth of the powder pattern, and the skew represents the asymmetry of the powder pattern. These conventions will be used throughout this thesis.

2.1.3 The direct magnetic dipole-dipole interaction

In the presence of a strong external magnetic field, the magnetic dipole moment associated with a nuclear spin angular momentum can be visualized as a tiny bar magnet, hence it produces a magnetic field around it. Any nucleus that resides in the vicinity of this tiny bar magnet will experience its magnetic field in addition to the much larger applied magnetic field.

The interaction between two tiny bar magnets can be described by a magnetic dipole-dipole interaction. The magnetic dipole-dipole interaction Hamiltonian can be readily derived from the classical expression and it has the following form (21):

$$\hbar^{-1} \mathcal{H}_{D} = 2\pi (A + B + C + D + E + F) R_{DD}$$
(2.13)

where

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$$A = -I_{1z}I_{2z} (3\cos^2\theta - 1)$$
 (2.14)

$$B = \frac{1}{4} \left(I_{1+}I_{2-} + I_{1-}I_{2+} \right) \left(3\cos^2\theta - 1 \right)$$
(2.15)

$$C = -\frac{3}{2} \left(I_{1z}I_{2+} + I_{1+}I_{2z} \right) \sin\theta \, \cos\theta \, \exp(-i\phi)$$
(2.16)

$$D = -\frac{3}{2} \left(I_{1z}I_{2-} + I_{1-}I_{2z} \right) \sin\theta \,\cos\theta \,\exp(i\phi)$$
(2.17)

$$E = -\frac{3}{4} I_{1+}I_{2+} \sin^2\theta \exp(-2i\phi)$$
 (2.18)

$$F = -\frac{3}{4} I_{1-}I_{2-} \sin^2\theta \exp(2i\phi)$$
 (2.19)

$$R_{DD} = \left(\frac{\mu_0}{4\pi}\right) \gamma_1 \gamma_2 \left(\frac{\hbar}{2\pi}\right) \left(\frac{1}{r^3}\right)$$
(2.20)

The terms A to F are known as the "dipolar alphabet" and R_{DD} is the direct dipolar coupling constant. The angles θ and ϕ are defined in Fig.2.5. In the presence of a strong magnetic field along the z direction, the dipolar alphabet is truncated, so that only the A and B terms remain for homonuclear spin pairs (Eq.(2.21)). It is, however, worth mentioning that the above truncation is valid only if the Zeeman interaction is much

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$$\hbar^{-1} \mathcal{H}_D = 2\pi (A + B) R_{DD} = -\pi R_{DD} (3 \cos^2 \theta - 1) (3I_{1z}I_{2z} - I_1 \cdot I_2) \quad (2.21)$$

larger than any other interactions involving the nuclear spins. In the presence of other strong interactions such as a quadrupole interaction, all other terms from C to F may be important. In this thesis, only spin- $\frac{1}{2}$ nuclei in situations where the Zeeman interaction indeed dominates will be considered.



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Figure 2.5 The direct magnetic dipole-dipole interaction between two magnetic dipole moments.

Since the direct magnetic dipole-dipole interaction is axially symmetric and traceless, there is only one independent variable within the three principal components, *i.e.*, $R_{11} = R_{22} = 3R_{DD}/2$ and $R_{33} = -3R_{DD}$. It is obvious that the unique axis of the principal axis system for the direct magnetic dipole-dipole interaction is along the internuclear vector. Similar to the anisotropic chemical shielding interaction, the direct magnetic dipole-dipole interaction is also dependent on the crystallite orientation with respect to the external magnetic field. Therefore, for a powder sample, a distribution of NMR frequencies or a powder pattern will result. A typical powder pattern arising from a dipolar interaction between two identical spin-¹/₂ nuclei is displayed in Fig.2.6.



Figure 2.6 A powder pattern due to the direct magnetic dipole-dipole interaction between two identical spin-¹/₂ nuclei.

It is readily seen that a direct magnetic dipole-dipole interaction depends on the magnetic moments of two interacting nuclear spins and their spatial separation. The magnitude of a dipolar interaction is expected to be large for nuclear species with a high magnetogyric ratio as well as for nuclei with a close spatial separation. By studying a direct magnetic dipole-dipole interaction, valuable structural information can be deduced. For example, one of the pioneering experiments in the early stage of NMR spectroscopy was performed by Pake (22). He measured the dipolar interaction between each pair of hydrogen nuclei in the water molecules of hydration in gypsum crystals (CaSO₄ \cdot 2H₂O),

from which the ¹H-¹H separation of 1.58 Å was obtained. Recent applications ut 'ring direct dipole-dipole interactions in spin pairs can be found in (23).

2.1.4 The indirect electron-mediated spin-spin interaction

Another type of nuclear spin interaction in NMR is that between nuclear spins transmitted *via* intervening electrons, namely the J interaction. In contrast to the direct magnetic dipole-dipole interaction, the J interaction is indirect, since it involves nucleuselectron interactions. The J interaction or indirect spin-spin interaction is more complicated than the three aforementioned nuclear spin interactions. In general, there are three mechanisms for an indirect spin-spin interaction: (*i*) the interaction between a nuclear spin and electron orbital angular momenta; (*ii*) the magnetic dipole-dipole interaction between a nuclear spin and electron spins; (*iii*) the Fermi contact interaction which arises from the fact that the s electrons have a non-zero probability of being found at the nucleus. Moreover, since the Hamiltonians describing the last two interactions do not commute, they do not have a common set of eigenfunctions. This results in mixing between their corresponding eigenstates, leading to a cross term that contributes to the indirect spin-spin interaction.

The indirect spin-spin interaction Hamiltonian can be written as:

$$\hbar^{-1} \mathcal{H}_{J} = 2\pi I_{1} \cdot J \cdot I_{2}$$
(2.22)

Again, the presence of a strong magnetic field truncates the total Hamiltonian and the secular Hamiltonian becomes:

$$\hbar^{-1} \mathcal{H}_{J} = 2\pi [J_{iso}I_{1} \cdot I_{2} + \frac{J_{zz} - J_{iso}}{2} (3I_{1z}I_{2z} - I_{1} \cdot I_{2}) + \frac{J_{xy} - J_{yx}}{2} (I_{1x}I_{2y} - I_{1y}I_{2x})]$$
(2.23)

where J_{iso} is the isotropic value of the J tensor in frequency units. Often J is assumed to be a symmetric tensor. Under these conditions, the last term in Eq.(2.23) vanishes. Regardless, this latter term does not contribute to the NMR line position in first order. A more detailed discussion concerning the anti-symmetric part of a J tensor can be found in Ref. (24). If a J tensor is further assumed to be axially symmetric with the unique axis being coincident with the internuclear vector, one has:

$$J_{zz} = \begin{bmatrix} \cos\theta & \sin\theta \\ 0 & 1 & 0 \\ -\sin\theta & 0 & \cos\theta \end{bmatrix} \begin{bmatrix} J_{\perp} & 0 & 0 \\ 0 & J_{\perp} & 0 \\ 0 & 0 & J_{\parallel} \end{bmatrix} \begin{bmatrix} \cos\theta & 0 & -\sin\theta \\ 0 & 1 & 0 \\ \sin\theta & 0 & \cos\theta \end{bmatrix} \end{bmatrix}_{zz}$$
(2.24)
$$= J_{\perp} \sin^2\theta + J_{\parallel} \cos^2\theta$$

Substituting Eq.(2.24) into Eq.(2.23), one obtains the spin Hamiltonian due to a symmetric J tensor:

$$\hbar^{-1} \mathcal{H}_{J} = 2\pi \left[J_{iso}I_{1} \cdot I_{2} + \frac{\Delta J}{3} \frac{3\cos^{2}\theta - 1}{2} \left(3I_{1z}I_{2z} - I_{1} \cdot I_{2} \right) \right]$$
(2.25)

where

$$\Delta J = J_{\parallel} - J_{\perp} \tag{2.26}$$

It is clear from Eqs.(2.21) and (2.25) that the spatial and spin dependence in the direct magnetic dipole-dipole and the J interaction Hamiltonians are similar. Therefore, it is usually difficult to separate a J tensor from a dipolar interaction tensor. That is, the experimental observable will be a combination of these two interactions. The experimental observable will be a simple quantity known as the effective dipolar coupling constant, R_{eff} .

$$R_{eff} = R_{DD} - \frac{\Delta J}{3} \tag{2.27}$$

Although numerous chemical applications have been made of the isotropic values of J interactions, much less is known about the anisotropy in J interactions. In fact, as long as the electronic environment at the nucleus deviates from spherical symmetry, the J interaction must be anisotropic. This can be readily appreciated when considering the similarity between chemical shielding and one of the mechanisms for J interactions, the spin-orbital mechanism. In the case of a chemical shielding, it is the external magnetic field that causes unquenching of the electron orbital angular momentum whereas, in the case of a J interaction, it is the field generated by the nuclear magnetic dipole moment that introduces unquenching of the electron orbital angular momentum. Since the electronic environment is not spherically symmetric, the degree of such unquenching will depend on the orientation of the nuclear magnetic moment in the molecule under study. Note that the orientation of the nuclear magnetic moment is always forced to align along the external magnetic field. Hence, the magnitude of a J interaction will depend on how

the molecule orients itself with respect to the external magnetic field.

2.2 Solid state NMR techniques

In the solid state, the absence of rapid molecular tumbling makes the observation of a high-resolution NMR spectrum very difficult. Usually it is helpful to make a distinction between abundant spin and dilute spin systems, since the NMR techniques involved in the two situations are quite different. Abundant spins are most often protons and rare spins are magnetically dilute nuclei such as ^{13}C , ^{31}P and ^{15}N nuclei. The difficulties that one faces in studying abundant spin systems are (a) the strong homonuclear dipole-dipole interactions and (b) the complexity of many-body spin systems. The NMR techniques used to obtain high-resolution spectra of abundant spins such as multiple-pulse sequences (25-27) and CRAMPS (combined rotation and multiple pulse spectroscopy) (27-29) will not be discussed here. Rather, only dilute spin-1/2 systems will be considered in this thesis.

2.2.1 High power abundant spin decoupling and magic-angle spinning

One major problem encountered in obtaining high-resolution NMR spectra of solids is the anisotropic nature of all nuclear spin interactions. Among the anisotropic interactions present in magnetically dilute spin systems, the heteronuclear dipole-dipole interaction between the dilute and abundant spins always gives rise to broad featureless NMR lineshapes, whereas other interactions will result in NMR lineshapes with some specific features. Usually the heteronuclear dipolar interaction between dilute and

abundant spins can be eliminated by applying strong RF radiation on the resonance frequency of abundant spins. The strong on-resonance RF radiation rapidly changes the spin state of the abundant spins and leads to spin decoupling. Under such conditions, the indirect spin-spin interaction between abundant and dilute spins is also eliminated by spin decoupling, since it is generally several orders of magnitude weaker than the direct dipolar interaction. Typical RF power required for sufficient decoupling of the ¹H-¹³C dipolar interaction is ca. 100 watts. The resultant decoupled NMR spectra of the rare spins will be exclusively determined by the chemical shielding, homonuclear dipolar and indirect spin-spin interactions among the rare spins. Although much information can be extracted from such a decoupled NMR spectrum, spectral overlap usually limits its usage to very simple spin systems.

In order to further eliminate the remaining anisotropic interactions (mainly anisotropic chemical shielding for dilute spins), another technique well-known as magicangle spinning (MAS) (7,8) must be employed. The MAS technique involves high-speed sample rotation about an axis inclined 54°44′ with respect to the external magnetic field. The rapid mechanical specimen rotation acts more-or-less like the molecular tumbling in isotropic liquids and results in solid state NMR spectra consisting of sharp peaks. For magnetically dilute spins, chemical shift anisotropy is usually very large. For example, ¹⁵N NMR frequencies due to the anisotropic nitrogen chemical shielding in *p*-nitroso-N,N-dimethylaniline cover a range of 1479 ppm (ca. 30 kHz at 4.70 T) (*30*). Typical sample spinning frequencies in modern NMR probes are below 15 kHz. If the sample rotation frequency is smaller than the frequency range that results from the anisotropic interactions, the central NMR peak will be flanked by a set of peaks (called spinning sidebands) with the separation between neighbouring peaks being equal to the specimen rotation frequency. Only when the rotation frequency is much greater than the anisotropic interactions (in frequency units) will all the spinning sidebands have negligible intensities.

As an example, Fig.2.7 shows several solid state ³¹P NMR spectra of $NH_4H_2PO_4$ under different conditions. It can be seen that without applying the abundant spin (proton) decoupling, the ³¹P NMR spectrum shows a broad peak, which is a result of anisotropic ³¹P chemical shift and heteronuclear dipolar coupling to protons (Fig.2.7a). When proton decoupling is applied, the ³¹P NMR spectrum becomes sharper and a typical powder pattern arising from anisotropic chemical shift is observed (Fig.2.7b). After applying the MAS technique with high-power ¹H decoupling, the ³¹P NMR spectra bear significantly higher resolution (Figs.2.7c and 2.7d).

2.2.2 Cross polarization

In 1972, Pines, Gibby and Waugh (10) demonstrated that NMR signals of dilute spins (¹³C nuclei) can be enhanced by transferring magnetization from the abundant spins (¹H nuclei) to the dilute spins. The technique termed as cross polarization (CP) has become a standard technique in obtaining solid state NMR spectra of dilute spins. The advantage of using CP is not only to enhance the NMR signals of dilute spins, but also to make the repetition time of the NMR experiment depend on the spin-lattice relaxation time of the abundant spins, which is often orders of magnitude shorter than that of the



Figure 2.7 Solid state ³¹P NMR spectra of NH₄H₂PO₄. (a) without ¹H decoupling;
(b) with high-power ¹H decoupling;
(c) high-power ¹H decoupling and MAS with spinning at 1543 Hz;
(d) high-power ¹H decoupling and MAS with spinning at 4024 Hz.

dilute spins. For instance, the ¹³C spin-lattice relaxation time in a crystalline alkane $C_{60}H_{122}$ is more than 1660 s (31). That is, one must wait for over 2 hours for the spin system to come to equilibrium after a $\pi/2$ pulse! On the other hand, the ¹H spin-lattice relaxation time is on the order of seconds. It is both of these two factors that make solid state NMR studies of dilute spins feasible. Nowadays the combination of CP, MAS and high-power abundant spin decoupling has become routine in NMR studies of chemical systems in the solid state.

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Chapter 3

NMR Spectra of Homonuclear Two-Spin Systems in Static Solids

3.1 Introduction

It has been shown in §2.1 that most nuclear spin interactions are anisotropic. In the liquid state, the rapid molecular tumbling motion averages all anisotropic interactions to the isotropic values, leading to high-resolution NMR spectra. For stationary polycrystalline or amorphous solids, since all possible orientations of crystallites are present in the sample, the resultant NMR spectra will be distributed over a large range of frequency. Such NMR spectra are called static powder spectra or simply powder patterns. Intensity distribution characteristics of powder patterns depend on particular nuclear spin interactions that are present in the spin system under investigation. Powder patterns due to either an anisotropic chemical shielding or a direct magnetic dipole-dipole interaction have been discussed in §2.1. In this chapter, the focus will be put on NMR lineshapes arising from homonuclear two-spin systems in which both of the interactions are present.

Interest in static NMR spectra of simple two-spin systems started in the early stages of NMR spectroscopy. As already mentioned, in 1948 Pake (22) discovered the magnetic dipole-dipole interaction between two nuclear spins and showed that important information concerning the internuclear distance can be derived directly from NMR spectra of either a single crystal or a powder sample containing "isolated" spin pairs. Pake's pioneering work has inspired numerous studies; however, attention of this chapter

will be restricted only to homonuclear spin pairs consisting of two magnetically dilute spin-¹/₂ nuclei such as ¹³C, ¹⁵N and ³¹P nuclei.

One of the main reasons for studying static NMR spectra of homonuclear two-spin systems is the possibility of obtaining the dipolar coupling constant between two spins, from which the internuclear distance can be derived. For a two-spin system consisting of two nuclei other than protons, chemical shift anisotropy is usually large thereby making a direct measurement of the dipolar coupling difficult. Several NMR techniques have been developed in order to remove the influence from chemical shift anisotropy. The Carr-Purcell spin-echo technique (32) is most often used for this purpose. By applying a 180° pulse at the midpoint of the evolution period, the dephasing of transverse magnetizations due to anisotropic chemical shifts can be refocused at the end of the evolution period. The most recent application along this line is the C-C bond length determination in the Buckminsterfullerene (C_{60}) molecule carried out by Yannoni and coworkers (33). Another useful technique for measuring internuclear distance between two homonuclear spins in static solids is the nutation NMR method also demonstrated by Yannoni and co-workers (34). Recently, the two-dimensional (2D) spin-echo technique was also used in determining dipolar couplings for static powder samples (35).

Another type of information available in NMR spectra of static solids is concerned with chemical shift tensors. VanderHart and Gutowsky (36) first studied solid-state NMR spectra arising from two-spin systems where both anisotropic chemical shift and dipolar interactions are present. They demonstrated that NMR spectra arising from a heteronuclear spin pair depend intimately on the mutual orientation of the chemical shift tensors and the dipolar tensor of the two spins. Since the dipolar tensor and the chemical shift tensor have a fixed geometric relationship in the molecular frame, from NMR spectra it is often possible to extract information concerning the orientation of chemical shift tensors in the molecular frame. This method has been known as the dependence chemical shift NMR method. In 1981, Zilm and Grant (37) extended this method to studies of homonuclear two-spin systems.

Surprisingly, since the early paper of Zilm and Grant (37), there have been scarcely any dipolar-chemical shift NMR studies involving homonuclear two-spin systems (35,38-40). This may be partly due to the intrinsically low sensitivity associated with NMR spectra of static solids and partly due to the complex features that may be present in static NMR spectra. As will be shown in this chapter, sensitivity is no longer a problem with modern NMR instrumentation. The objective of this chapter is to present a detailed study of dipolar-chemical shift NMR spectra arising from different types of homonuclear two-spin systems. To demonstrate the great potential of using the dipolarchemical shift NMR method, a number of homonuclear spin-pair systems involving ¹³C, ¹⁵N and ³¹P nuclei in several important classes of compounds will be investigated, from which valuable information concerning the orientation of chemical shift tensors will be obtained. The remainder of this chapter will be organized as follows. General theoretical expressions to describe static NMR spectra of a homonuclear two-spin system will be given in §3.2. Three different special cases will be studied in §3.3, §3.4 and §3.5, respectively. Experimental details will be given in §3.6 and, finally, a brief summary will appear in §3.7.

3.2 Theory

For an "isolated" spin-pair system containing two spin-1/2 nuclei, the spin Hamiltonian in the presence of a strong external magnetic field contains the following terms:

$$\mathcal{H} = \mathcal{H}_{Z} + \mathcal{H}_{CS} + \mathcal{H}_{D} + \mathcal{H}_{J}$$
(3.1)

where \mathcal{H}_z is the nuclear Zeeman interaction, \mathcal{H}_{cs} is the chemical shielding interaction, \mathcal{H}_D is the direct magnetic dipole-dipole interaction and \mathcal{H}_J is the indirect spin-spin (*J*) interaction. For a particular crystallite, the spin Hamiltonian is given by Eq.(3.2).

$$\mathcal{H} = -\omega_1 I_{1z} - \omega_2 I_{2z} + \omega_J I_1 \cdot I_2 + \omega_D (3I_{1z}I_{2z} - I_1 \cdot I_2)$$
(3.2)

where ω_i (*i*=1 and 2) describes the NMR frequency due to the nuclear Zeeman interaction and chemical shielding for spins 1 and 2, respectively, ω_D describes the NMR frequency due to the dipolar interaction and ω_J is indirect spin-spin coupling constant. It is most convenient to choose the dipolar interaction tensor as a reference frame, denoted as (r_{XX} , r_{YY} , r_{ZZ}), with the internuclear vector along the z axis; see Fig.3.1. Under this condition, one has

$$\omega_1 = \omega_0 \left[1 - \left(\sigma_{11}^1 \cos^2 X_1 + \sigma_{22}^1 \cos^2 Y_1 + \sigma_{33}^1 \cos^2 Z_1 \right) \right]$$
(3.3)

$$\omega_2 = \omega_0 \left[1 - \left(\sigma_{11}^2 \cos^2 X_2 + \sigma_{22}^2 \cos^2 Y_2 + \sigma_{33}^2 \cos^2 Z_2 \right) \right]$$
(3.4)

$$\omega_D = 2\pi R_{eff} \frac{(1-3\cos^2\theta)}{2}$$
(3.5)

where θ is the angle between the external magnetic field and the z axis, $\cos X_i$, $\cos Y_i$ and $\cos Z_i$ are directional cosines that define the direction of external magnetic field in the



Figure 3.1 The orientation of a chemical shielding tensor in the dipolar tensor frame. Since the dipolar tensor is axially symmetric, the choice of r_{XX} and r_{YY} is arbitrary.

principal-axis-system of the chemical shielding tensor. Usually a set of Euler angles $(\alpha^{CS}, \beta^{CS}, \gamma^{CS})$ is used to define the chemical shielding tensor in the reference frame; see Fig.3.1. The external magnetic field is defined by the polar angle θ_D and the azimuthal angle ϕ_D in the dipolar tensor reference frame. Therefore, the directional cosines (cos X_i , cos Y_i , cos Z_i) can be readily related to the direction of the external field by Eq.(3.6).

$$\begin{cases} \cos X_{i} \\ \cos Y_{i} \\ \cos Z_{i} \end{cases} = \Re^{-1} (\alpha_{i}^{CS}, \beta_{i}^{CS}, \gamma_{i}^{CS}) \begin{pmatrix} \sin \theta_{D} \cos \phi_{D} \\ \sin \theta_{D} \sin \phi_{D} \\ \cos \theta_{D} \end{pmatrix}$$
(3.6)

where \Re is a unitary transformation and it has the form:

$$\Re (\alpha, \beta, \gamma) = \cos\alpha \cos\beta \cos\gamma - \sin\alpha \sin\gamma \quad \sin\alpha \cos\beta \cos\gamma + \cos\alpha \sin\gamma \quad -\sin\beta \cos\gamma -\cos\alpha \cos\beta \sin\gamma - \sin\alpha \cos\gamma \quad -\sin\alpha \cos\beta \sin\gamma + \cos\alpha \cos\gamma \quad \sin\beta \sin\gamma \cos\alpha \sin\beta \quad \sin\alpha \sin\beta \quad \cos\beta$$

$$(3.7)$$

Note that the superscript CS has been omitted in the above matrix for clarity. As shown in Appendix II, the frequencies and intensities of the resultant NMR lines are:

$$\omega^{1} = \frac{1}{2} (\omega_{1} + \omega_{2} + \omega_{J} + 2\omega_{D} + D), \qquad P_{1} = 1 - \frac{\omega_{J} - \omega_{D}}{D}; \qquad (3.8)$$

$$\omega^{2} = \frac{1}{2} (\omega_{1} + \omega_{2} - \omega_{J} - 2\omega_{D} + D), \qquad P_{2} = 1 + \frac{\omega_{J} - \omega_{D}}{D}; \qquad (3.9)$$

$$\omega^{3} = \frac{1}{2}(\omega_{1} + \omega_{2} + \omega_{J} + 2\omega_{D} - D), \qquad P_{3} = 1 + \frac{\omega_{J} - \omega_{D}}{D}; \qquad (3.10)$$

$$\omega^{4} = \frac{1}{2} (\omega_{1} + \omega_{2} - \omega_{j} - 2\omega_{D} - D), \qquad P_{4} = 1 - \frac{\omega_{j} - \omega_{D}}{D}; \qquad (3.11)$$

where

$$D = [(\omega_1 - \omega_2)^2 + (\omega_J - \omega_D)^2]^{1/2}$$
(3.12)

The above equations indicate that, for a particular crystallite, the NMR spectrum exhibits four lines. Because of the presence of both dipolar and J interactions, the four-line spectrum for a given crystallite is more complicated than the well-known "AB" spectra

in solution state NMR studies. Furthermore, since ω_1 , ω_2 and ω_D in Eqs.(3.8)-(3.12) are orientation dependent, NMR spectra for different crystallites will vary as a function of the individual crystallite orientation with respect to the external magnetic field. Therefore, the resultant NMR spectrum for a powder sample will contain a large number of four-line subspectra. In other words, each transition given in Eq.(3.8)-(3.11) will in fact describe a powder lineshape; the resultant NMR spectrum consists of four powder lineshapes.

In general cases, it is not possible to derive analytical expressions to describe each of the four subspectra; numerical calculations are necessary. However, in some special situations, analysis of static NMR spectra can be simplified. In this chapter, three cases will be considered. First, when the chemical shift difference between the two spins is always zero at all crystallite orientations, *i.e.*, $\omega_1 = \omega_2$, the two spins are said to be magnetically equivalent (26). Such a two-spin system is denoted as an A_2 spin system. Second, if the chemical shift difference between the two spins is always much greater than the spin-spin interactions at all crystallite orientations, i.e., $|\omega_1 - \omega_2| \ge \omega_J, \omega_D$, the two homonuclear spins are said to constitute an AX spin system. Third, when the chemical shift difference between the two spins is comparable to the spin-spin interactions at some crystallite orientations, i.e., $\omega_1 - \omega_2 \sim \omega_J$, ω_D , the two spins constitute an AB spin system. These definitions of A2, AX and AB spin systems are somewhat similar to those in solution NMR studies; however, as will be shown, the resultant static NMR spectra for a powder sample will be much more complicated. The complexity results mainly from the fact that ω_1 , ω_2 and ω_D are orientation dependent in solids and, therefore, the resultant NMR spectrum will be a "mixture" or sum of a large number of AX, AB and A_2 spectra.

3.3 NMR spectra of A₂ spin systems

In this section, special cases where the two nuclei in a spin pair are *magnetically* equivalent will be considered. Under this condition, the four resonances given in Eqs.(3.8)-(3.11) are reduced to two with equal intensity; Eq.(3.13).

$$\omega^{\pm} = \omega_{CS} \pm \frac{3}{2}\omega_D \tag{3.13}$$

where $\omega_{CS} = \omega_1 = \omega_2$. Clearly, this equation does not contain ω_J , indicating that the J coupling between two magnetically equivalent spins is not observable. It is also seen in Eq.(3.13) that the static NMR spectrum of an A₂ spin system consists of only two powder lineshapes. It is straightforward to show that each of the two subspectra in the static NMR spectrum of an A₂ spin system has the same characteristic lineshape as that arising from an isolated spin with anisotropic chemical shift (37). That is, each of the two lineshapes can be characterized by three *effective* principal components denoted as T_i^{\pm} (i = 1, 2, and 3) (41).

3.3.1 Phosphorus chemical shift tensors in dithiadiphosphetane disulfides

The ³¹P NMR spectra of two different dithiadiphosphetane disulfides, 1 and 2, were studied. The Lawesson reagent, 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (1), is often used for thiation of ketones, carboxamides,

esters, lactones, lactams, imides, enamines and S-substituted thioesters (42). The crystal structure of 1 indicates that the two phosphorus atoms are related by an inversion centre (43), hence, the two ³¹P nuclei in 1 are *magnetically* equivalent. Under the condition of high-power proton decoupling, the two ³¹P nuclei in 1 constitute an isolated A_2 spin pair.



Only recently has use been made of dipolar-chemical shift NMR spectra of ${}^{31}P$ spin pairs in determining chemical shift tensor orientations (35). The objective of this section is to demonstrate that, even when two ${}^{31}P$ nuclei are not directly bonded, the small dipolar coupling between them can still have significant influences on static NMR spectra.

The MAS and static ³¹P NMR spectra of 1 are shown in Fig.3.2. In the MAS spectrum, the isotropic peak is found at 41.49 ppm, flanked by many spinning sidebands, which indicates a significant chemical shift anisotropy at the ³¹P nucleus. Indeed, the static spectrum spans about 400 ppm. Clearly, the static spectrum consists of two subspectra, which is typical for an A_2 spin system, as previously mentioned.

In principle, the two dipolar subspectia observed in the static NMR spectrum of 1 can be simulated using Eq.(3.13). However, if $|\omega_{ii} - \omega_{jj}| \ge 2\pi R_{eff}$, a more straightforward method can be applied. Under this condition, the differences or the splittings at the effective principal components, T_i^{\pm} , are directly related to the orientation



Figure 3.2 MAS (top) and static (bottom) ³¹P NMR spectra of the Lawesson's reagent, 1, at 4.70 T. In the static spectrum, 512 transients were recorded and the recycle time was 10 s.

of the chemical shift tensor with respect to the internuclear vector. The relationship is:

$$\Delta T_i = T_i^+ - T_i^- = \frac{3}{2} R_{eff} (1 - 3 \cos^2 \phi_{ii}), \quad i = 1, 2, 3.$$
 (3.14)

where ϕ_{ii} is the angle between the internuclear vector and δ_{ii} .

In general, three splittings can be measured directly from experimental NMR spectra. However, it is clear that the three equations in Eq.(3.14) are not independent, *i.e.*,

$$\sum_{i=1}^{3} \Delta T_i = 0 \tag{3.15}$$

Therefore, one is encountered with a problem that may have an infinitive number of solutions. Usually, the symmetry that the molecule of interest possesses may help limit the number of solutions. In case 1, the molecule contains a mirror plane defined by two phosphorus atoms and two terminal sulphur atoms, $S=P \cdot \cdot \cdot P=S$. Hence, one of the three principal components must lie perpendicular to the mirror plane. Under this condition, because of the constraint given by Eq.(3.15), the possibility for the component with the smallest splitting being perpendicular to the mirror plane can be ruled out. Therefore, the number of acceptable solutions is reduced to two.

From the static NMR spectrum of 1, the three splittings are measured as 1853, 1075 and 732 Hz at δ_{11} , δ_{22} and δ_{33} , respectively. The error in these splittings is estimated to be \pm 50 Hz. The two possible solutions for the phosphorus chemical shift tensor orientations are: (1) the δ_{11} component is perpendicular to the molecular mirror

plane and (2) the δ_{22} component is perpendicular to the mirror plane. For the first solution, one has $R_{eff} = 1235$ Hz, which corresponds to a P-P separation of 2.52 Å, and the orientation of the phosphorus chemical shift tensor is given by $\phi_{11} = 90^\circ$, $\phi_{22} =$ 43°, and $\phi_{33} = 47^{\circ}$. For the second solution, $R_{eff} = 717$ Hz, which corresponds to r_{PP} = 3.02 Å, and $\phi_{11} = 19^{\circ}$, $\phi_{22} = 90^{\circ}$, and $\phi_{33} = 71^{\circ}$. Purely from the viewpoint of NMR spectra, the two solutions are identical. Therefore, arguments based on results from other studies must be used to differentiate between these two solutions. First, based on the crystal structure of 1, the P-P separation is 3.08 Å (43). Hence, the second solution clearly yields a reasonable P-P distance whereas the P-P separation derived from the first solution is remarkably short. Second, a close examination of the orientation of the phosphorus chemical shift tensor also favours the second solution. According to the second solution, the most shielded component, δ_{33} , is close to the P=S bond, which is in agreement with the results found in phosphine sulfides as studied by single-crystal NMR methods (44,45). Therefore, the first solution is discarded and the resultant orientation of the phosphorus chemical shift tensor in 1 is depicted in Fig.3.3.



Figure 3.3 The orientation of the phosphorus chemical shift tensors in the Lawesson's reagent, 1.

Compound	$\delta_{ m iso}$	δ_{11}	δ_{22}	δ ₃₃	Ω	κ	R _{eff}	-
1	41.49	184	138	-197	381	0.25	717	
2	39.13	192	131	-205	397	0.23	841	

Table 3.1Phosphorus chemical shift tensors* and effective dipolar coupling
constants* in 1 and 2

^aAll chemical shifts are in ppm and are accurate to ± 2 ppm. ^bEffective dipolar coupling constants are in Hz and are accurate to ± 50 Hz.

A related compound known as the Davy's methyl reagent, 2,4-bis(methylthio)-1,3dithia-2,4-diphosphetane-2,4-disulfide (2), was also studied using the same procedure. The results are also listed in Table 3.1. For this compound, it is interesting to note that the P-P separation is 2.86 Å, shorter than that in 1 by 0.16 Å. This is in agreement with the P-P separation in the related compound, methyl metadithiophosphonate, $[CH_3 \cdot PS_2]_2$, in which $r_{PP} = 2.906$ Å (46). It is, however, not surprising that the orientations of the phosphorus chemical shift tensors in these two closely related compounds are identical.

3.3.2 Olefinic carbon chemical shift tensors in *trans*-stilbene and

$Pt(\eta^2$ -trans-stilbene)(PPh₃)₂

Clearly, the shortcut approach by using Eq.(3.14) as demonstrated in §3.3.1 is valid only when $|\omega_{ii} - \omega_{jj}| \ge 2\pi R_{eff}$. If this condition is not satisfied, one must perform numerical calculations using Eq.(3.13). In this section, two general cases where R_{eff} is large will be investigated. The objective of the study outlined here is to determine the olefinic carbon chemical shift tensors in *trans*-stilbene- α , β -¹³C₂ (3) and its zerovalent platinum complex, $Pt(\eta^2$ -trans-stilbene- α,β -¹³C₂)(PPh₃)₂ (4). In both compounds, the *trans*-stilbene molecules are doubly ¹³C-labelled at the olefinic carbons, hence, the two directly bonded ¹³C nuclei constitute a homonuclear two-spin system in each of the two compounds.



Surprisingly, although for twenty years ¹³C chemical shift of olefinic carbons has been used extensively in studying numerous metal-olefin complexes in solutions (47), only two solid-state ¹³C NMR studies have appeared dealing with olefinic carbon chemical shift *tensors* in metal-olefin complexes. Wallruff studied solid state ¹³C NMR spectra of a series of metal-olefin and metal-diene complexes from which principal components of the olefinic carbon chemical shift tensors were obtained (48). In a more recent study, Butler and co-workers (49) reported the principal components of the olefinic carbon chemical shift tensor in Zeise's salt and Zeise's dimer. However, these two studies yielded only the magnitudes of the principal components of olefinic carbon chemical shift tensors; to date no olefinic carbon chemical-shift tensor has been *fully* determined for any transition-metal olefin complex. It is however noted that Ellis and co-workers have recently reported carbon chemical shift tensors for ethylene molecules adsorbed on a Ag/γ -alumina surface (40).

Olefinic carbon chemical shift tensors in trans-stilbene. The crystal structure of trans-stilbene has been determined by X-ray crystallography (50). The crystals are monoclinic (space group $P2_1/c$). There are two crystallographically non-equivalent

molecules lying at inversion centres of the unit cell and one of the two independent molecules exhibits orientational disorder. Therefore, the two olefinic carbons in each of the two molecules can be treated as an A_2 spin system. Since the two distinct molecules are very nearly related by a twofold screw axis parallel to **a**, it is not surprising that the olefinic carbons of the two molecules in **3** give rise to identical isotropic chemical shift in the ¹³C CP/MAS spectrum (Fig.3.4a).

For free *trans*-stilbene molecules, the isotropic ¹³C chemical shift of the olefinic



Figure 3.4 Carbon-13 MAS NMR spectra of (a) *trans*-stilbene, 3, and (b) $Pt(trans-stilbene)(PPh_3)_2$, 4, at 9.40 T.

carbons is found to be 128 ppm. However, on coordination to platinum(0), the isotropic peak of the olefinic carbons is shifted to 68 ppm (Fig.3.4b). This increase in olefinic carbon shielding on coordination to a metal is in agreement with all previous observations based on solution state ¹³C NMR studies. This trend is also obvious in two previous solid state ¹³C NMR studies of metal-olefin complexes (48,49). For example, the isotropic ¹³C chemical shift of the ethylene ligand in Zeise's salt, K^+ [PtCl₃(C₂H₄)]⁻·H₂O, was found to be 60 ppm more shielded than that of a free ethylene ligand (49). In Fig.3.4 it is also clear that the spinning sidebands in the ¹³C MAS NMR spectrum of 3 are more intense than those in the spectrum of 4, indicating that the chemical shift anisotropy of olefinic carbons is considerably reduced on coordination to Pt(0) (vide infra).

In the ¹³C CP/MAS spectrum of 4, a broad peak is observed, flanked by weak spinning sidebands. The full-width at the half-height of the peak due to the "olefinic" carbon in the ¹³C CP/MAS spectrum of 4 is 300 Hz at 4.70 T, which is much greater than that of the corresponding peak in 3, 120 Hz. The ¹³C CP/MAS spectrum of 4 obtained at 9.40 T exhibits essentially identical features except that a slightly greater linewidth is observed, 390 Hz. The line broadening mechanism in ¹³C CP/MAS spectra of 4 is still not clear. However, it is noted that, in the previous solid state ¹³C NMR study of Zeise's salt and Zeise's dimer, broad peaks were also observed in ¹³C CP/MAS spectra (*49*). Presumably, the bulk magnetic susceptibility of a metal-olefin complex is quite different from that of a free organic ligand.

In Fig.3.5 the ¹³C static NMR lineshape of 3 at 4.70 T is shown together with



Figure 3.5 Static ¹³C NMR spectra of *trans*-stilbene, **3**, at 4.70 (top) and 9.40 T (bottom). Top: number of transients, 512; recycle time, 100 s. Bottom: number of transients, 512; recycle time, 120s.

the calculated spectrum. Since the two dipolar-coupled olefinic carbons in each of the two distinct *trans*-stilbene molecules are related by the inversion centre symmetry, they can be treated as an A_2 spin system. Clearly, the static ¹³C NMR lineshape of **3** consists of two dipolar subspectra as mentioned previously. The static ¹³C NMR lineshape of **3** was also obtained at 9.40 T and the resultant spectrum is shown in Fig.3.5 with the best-fit calculated spectrum.

It is well-known that *trans*-stilbene and *trans*-azobenzene are isostructural and both exhibit the same kind and degree of disorder (50). However, in contrast to transazobenzene (39) where different nitrogen chemical shift tensors have been observed for the two crystallographically non-equivalent molecules in the unit cell, there is no detectable difference in the olefinic carbon chemical shift tensors between the two independent *trans*-stilbene molecules. One possible explanation for the discrepancy in trans-stilbene and trans-azobenzene may be that nitrogen chemical shift tensors in transazobenzene are more sensitive to subtle structural differences between the two distinct Therefore, one single set of parameters was assumed for the two crystallosites. graphically non-equivalent trans-stilbene molecules. Good agreement between the observed and calculated spectra at two fields (Figs.3.5) indicates that this is a reasonable assumption. Analyses of the static ${}^{13}C$ NMR spectra of a static powdered sample of 3 at two fields, 4.70 and 9.40 T, yield the following principal components of the olefinic carbon chemical shift tensors: $\delta_{11} = 215$, $\delta_{22} = 120$ and $\delta_{33} = 49$ ppm. These values are accurate to ± 2 ppm. It is known that the most shielded component, δ_{33} , of olefinic carbon chemical shift tensors is always nearly perpendicular to the HC=CH plane.

Hence, this component is fixed to the normal of the HC=CH plane during the simulation process. Analyses also indicate that the least shielded component, δ_{11} , is almost perpendicular to the C=C bond lying in the HC=CH plane. The angle between δ_{11} and the C=C direction is 85 ± 5°. This places the intermediate component, δ_{22} , approximately along the C=C bond also lying in the HC=CH plane. These tensorial orientations are in excellent agreement with the results for olefinic carbons in *trans*dihydromuconic acid (HOOCCH₂CH=CHCH₂COOH) determined by a single-crystal NMR study (51). The ¹³C-¹³C dipolar coupling constant used in the calculated spectra is 2.80 ± 0.08 kHz, corresponding to $r_{CC} = 1.39 \pm 0.02$ Å. This NMR-derived internuclear distance is somewhat longer than those determined by X-ray crystallography possibly due to motional averaging (37). Because of the limited accuracy in the static NMR lineshapes, an overall ¹³C-¹³C dipolar coupling constant was used in the calculations despite the fact that two types of *trans*-stilbene molecules are present in the unit cell with one of the two molecules being orientationally disordered.

Olefinic carbon chemical shift tensors in $Pt(\eta^2$ -trans-stilbene)(PPh₃)₂. It is wellknown that significant structural differences exist between Pt(0)- and Pt(II)-olefin complexes (52). First, in the Pt(II)-olefin complexes, the olefin double bond always lies approximately perpendicular to the square plane containing the platinum atom and other ligands; however, in Pt(0)-olefin complexes, the C=C bond lies nearly in the plane. Second, the C=C double bond of the olefin ligand is only weakened slightly on coordination to Pt(II) whereas a considerable C=C bond lengthening is involved on coordination to Pt(0).

The crystal structure of (trans-stilbene)bis(tri-p-tolylphosphine)nickel(0), a complex closely related to 4, indicates that the *trans*-stilbene ligand possesses an approximate C_2 symmetry (53). This implies that the chemical shift tensors for the two olefinic carbons in this stilbene-nickel complex must also be related by the C_2 symmetry. It is also noted that, in this complex, although the C=C bond length, 1.471 Å, is considerably longer than that in the free ligand, 1.327 Å, the trans arrangement remains and the planarity of the Cipso-C=C-Cipso moiety is modified slightly from that of the free trans-stilbene ligand. This can be seen by considering the fact that the $C_{ipso}(1)$ -C(1)=C(2) and $C(1)=C(2)-C_{ipso}(2)$ interplanar angle is only 17.3°. This approximate C_2 symmetry also exists in 4,4'-dinitro-(*trans*-stilbene)bis(triphenylphosphine)platinum (54). Therefore, it may be reasonable to assume that the two olefinic carbon chemical shift tensors in 4 are also related by a C_2 symmetry. For the free trans-stilbene ligand, the δ_{33} component was found to lie along the C_2 axis. Since the C_2 axis is the direction pointing to the metal centre, the chemical shielding along this direction is most insensitive on going from the free ligand to the complex. Indeed, the low-frequency ends of the ¹³C static NMR spectra of 3 and 4 are approximately the same, indicating that the δ_{33} components of the carbon chemical shielding tensors in 4 remain along the molecular C_2 axis. Therefore, δ_{33} components of the two tensors become coincident whereas other components of the two tensors are related by the C_2 symmetry. Recently, it has been demonstrated that, for spin-pair systems in which the chemical shift tensors for the two coupled spins are related by a C_2 axis, distinct AB features are usually expected in static NMR spectra (30,55). In contrast, inspection of the ¹³C NMR spectra shown in Fig.3.6


Figure 3.6 Carbon-13 static NMR spectra of Pt(*trans*-stilbene-¹³C₂)(PPh₃)₂, 4, at 4.70 (top) and 9.40 T (bottom). Top: number of transients, 880; recycle time, 60 s. Bottom: number of transients, 6000; recycle time 10s.

indicates no AB feature. This observation suggests that the two chemical shift tensors in 4 must be in such a special case that they are nearly coincident. In other words, the two dipolar-coupled ¹³C nuclei in 4 can be approximated as an A₂ spin pair. In Fig.3.6 the static ¹³C NMR lineshapes of 4 obtained at 4.70 and 9.40 T are displayed together with the calculated spectra. The calculated spectra are in reasonable agreement with the observed ones, indicating that treating the spin system in 4 as an A₂ spin system is a reasonable assumption. The parameters used in the calculation are: $\delta_{11} = 80$, $\delta_{22} = 73$ and $\delta_{33} = 50$ ppm. The errors in these values are estimated to be ± 2 ppm. The orientations of the olefinic carbon chemical shift tensors in 4 are depicted in Fig.3.7 together with those in 3 for comparison. The effective ¹³C-¹³C dipolar coupling constant



Figure 3.7 Approximate orientations of the olefinic carbon chemical shift tensors in (A) *trans*-stilbene, **3**, and in (B) Pt(*trans*-stilbene)(PPh₃)₂, **4**.

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used in the calculation is 2.60 ± 0.08 kHz, which corresponds to a C-C separation of 1.42 ± 0.02 Å. This NMR-derived bond length is comparable to the "C=C" bond distance, 1.416 Å, reported for 4,4'-dinitro-(*trans*-stilbene)bis(triphenylphosphine)-platinum (54).

Interestingly, in contrast to the tensorial orientations in the free stilbene ligand, the least shielded component, δ_{11} , in **4** is found to lie along the C=C bond and the intermediate component lies perpendicular to the C=C bond. In the free stilbene ligand, the span of the olefinic carbon chemical shift tensor is 166 ppm, but it is reduced to only 30 ppm on coordination to Pt(0). Inspection of the individual principal components reveals that such a large reduction in chemical shift anisotropy on coordination results from shielding increases only along δ_{11} and δ_{22} directions. The largest shielding increase is found along the direction perpendicular to the Pt-C-C plane, *i.e.*, δ_{11} (free ligand) - δ_{22} (complex) = 142 ppm. This increase contributes over 78% of the shielding increase in the isotropic chemical shift. As expected, the most shielded component, δ_{33} , remains unchanged on coordination to Pt(0).

Discussion. It is noted that data on olefinic carbon chemical shift tensors for platinum-olefin complexes are extremely limited in the literature. To date only three Pt(II)-olefin complexes have been characterized by solid state ¹³C NMR spectroscopy and no report on olefinic carbon chemical shift tensors of Pt(0)-olefin complexes has appeared. The olefinic carbon chemical shift tensors in related platinum-olefin complexes are listed in Table 3.2.

From Table 3.2, it is found that the isotropic chemical shift of olefinic carbons

Compound	Metal	$\delta_{ m iso}$	δ ₁₁	δ ₂₂	δ ₃₃	Ω	κ
Pt(COD)Cl ₂ ^c	Pt(II)	101	185	112	3	182	0.18
		(128)	(238)	(126)	(21)	(217)	-0.03
$K^{+}[Pt(ethylene)Cl_{3}]^{-} \cdot H_{2}O^{d}$	Pt(II)	63	135	67	-10	145	0.08
		(123)°	(234)	(120)	(24)	(210)	-0.04
<i>trans</i> -[{PtCl ₂ (ethylene)} ₂] ^d	Pt(II)	77	157	84	-14	171	0.12
		(123)°	(234)	(120)	(24)	(210)	-0.04
Pt(<i>trans</i> -stilbene)(PPh ₂) ¹	Pt(0)	68	80	73	50	30	0.50
		(128)	(215) (120)	(49)	(166)	-0.14

Table 3.2. Olefinic carbons chemical shift tensors in zerovalent and Divalent platinum-olefin complexes^{a,b}

*All chemical shifts are in ppm.

^bChemical shift data for corresponding free olefin ligands are listed in parenthesis.
^cCOD = 1,5-cyclooctadiene, Ref.(48).
^dRef.(49).
^eRef.(37).
^fThis work.

in all platinum-olefin complexes shifts towards the low-frequency (more shielded) direction as compared with the corresponding values in free olefin ligands. However, some discrepancies exist between Pt(II)- and Pt(0)-olefin complexes. First, for the Pt(II)- olefin complexes, such a shift results from shielding increases at all three components whereas for the Pt(0)-stilbene complex it results from shielding increases only at δ_{11} and δ_{22} components. Second, the chemical shift anisotropy in the Pt(0)-stilbene complex is

considerably smaller than those in the Pt(II)-olefin complexes. Third, although the isotropic coordination shifts are comparable for the Pt(II) and Pt(0) complexes listed in Table 3.2, the shielding change at the δ_{11} component is significantly greater in the Pt(0) complex than in the Pt(II) complexes.

Since the δ_{33} component of the olefinic carbon chemical shift tensors is associated only with the $\sigma \rightarrow \sigma^*$ excitations of the olefin ligand, an unchanged δ_{33} observed for the Pt(0)-stilbene complex indicates that the $\sigma \rightarrow \sigma^*$ energy gap remains approximately unchanged on coordination to Pt(0). On the other hand, this energy gap is modified to a greater extent when the olefin ligands are in coordination to Pt(II). This seems puzzling since the C=C bond distance is lengthened to a greater extent in Pt(0)-olefin complexes (52). Probably the discrepancy found in δ_{33} components is related to the different geometric orientations of the olefin ligand in the two types of complexes. However, a further discussion is restricted due to the lack of data.

The bonding in transition metal-olefin complexes is generally described as consisting of electron donation of the olefin π orbital to the metal and electron acceptance from the metal into olefin π^* orbital (back bonding) (52). In an early solution state ¹³C NMR study, Clark and co-workers attributed the isotropic coordination chemical shift to the metal back bonding to π^* (56). Clearly, it will be more informative to study individual principal components of a chemical shift tensor than the isotropic chemical shift alone. As was noted earlier, the reduction of the olefinic carbon chemical shift anisotropy is largely due to a shielding increase along the direction perpendicular to the plane containing Pt and the two olefinic carbons. In free *trans*-stilbene ligands, the

remarkable deshielding along this direction ($\delta_{11} = 215$ ppm) is due to the small energy gaps associated with $\sigma \rightarrow \pi^*$ circulations. It is found that, when bonding to the Pt(0) metal, the energy gaps associated with $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ of the olefin ligand are significantly increased. Since the metal to π^* back bonding ability increases in the order Pt(0) > Rh(I) > Pt(II) (57), it is reasonable that a much greater shielding increase is observed in the Pt(0)-olefin complex than in the Pt(II)-olefin complexes, as is apparent in Table 3.2.

As already mentioned, data on carbon chemical shift tensors for oganometallic compounds are very limited. Possible extentions of the work outlined here would be of obvious interest. For example, it will be interesting to compare olefinic carbon chemical shift tensors in *cis*-stilbene with the *trans* isomer as well as the corresponding complexes. Further studies of Pt(II) or Pt(0) complexes containing other alkenes and alkynes will be necessary. More sophisticated molecular orbital calculations on carbon shielding tensors in organometallic compounds will also be a challenge.

3.3.3 The magic orientation

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In §3.3.1 and §3.3.2, static NMR spectra of several different A_2 spin systems have been studied. This section will be focused on a very special case. As predicted in Eq.(3.14), there exists a special situation where all three splittings vanish, *i.e.*, $\Delta T_i =$ 0 (*i* = 1, 2, and 3). Clearly, such a situation corresponds to a dipolar vector with three directional cosines being cos $\phi_{11} = \cos \phi_{22} = \cos \phi_{33} = (1/3)^{1/2}$. Since this special direction makes three "magic" angles with respect to the three principal components of the chemical shift tensor, this orientation is referred to as the magic orientation in this thesis. Obviously, if the three principal components of a chemical shift tensor are expressed as the three edges of a cube, the magic orientation represents the diagonal line of the cube, *i.e.*, the (111) direction, as depicted in Fig.3.8. According to Eq.(3.14),



Figure 3.8 The magic orientation.

for an A_2 system where the dipolar vector lies along the magic orientation, the NMR spectrum will show no splitting at any of the three principal components. In other words, regardless of the dipolar coupling between the two spins, the static NMR spectrum of such an A_2 system will be similar to that of an isolated spin!

To date there has been no reported observation on a magic-orientation arrangement in any compound; however, it was found that the ${}^{31}P{}^{-31}P$ vector in tetraethyl diphosphine disulfide (5) lies quite close to the magic orientation in the principal-axisframe of the phosphorus chemical shift tensor. The crystal structure of 5 (P1, Z=1) indicates that the two directly bonded phosphorus atoms are related by a centre of inversion (58), hence, the two ³¹P nuclei constitute an A_2 spin system. The static ³¹P NMR spectrum of 5 is shown in Fig.3.9. Surprisingly, in spite of a large dipolar



Figure 3.9 Phosphorus-31 static NMR spectrum of tetraethyl diphosphine disulfide, 5, at 4.70 T. Number of transients, 32; recycle time, 30s.

coupling constant between the two directly bonded ³¹P nuclei in 5 (ca. 1.7 kHz, which corresponds to a maxium splitting of 5.1 kHz), two rather small splittings were observed in the static ³¹P NMR spectrum, $\Delta T_2 = 1021$ and $\Delta T_3 = 1232$ Hz. The splitting at the T_1 region is too small to be resolved; however, the constraint of Eq.(3.15) requires ΔT_1 = 211 Hz. Since the only molecular symmetry is the centre of inversion at the midpoint of the P-P bond, it is not possible to reduce the number of solutions without the knowledge of the dipolar coupling constant. To measure the dipolar coupling constant between the two ³¹P nuclei in 5, a 2D spin-echo experiment (35) was carried out. The 2D ³¹P spin-echo spectrum is shown in Fig.3.10, from which the effective dipolar coupling constant, R_{eff} , is measured to be 1.68 ± 0.05 kHz. If no motional correction is made, this observed effective dipolar coupling constant corresponds to $\Delta^{1}J(^{31}P,^{31}P)$ = 0.3 kHz, based on r_{PP} = 2.22 Å which was determined by an X-ray diffraction study



Figure 3.10 Phosphorus-31 2D spin-echo NMR spectrum of tetraethyl diphosphine disulfide, 5, at 4.70 T.

for 5 (58). The implication of this result is that neither anisotropy in ${}^{1}J({}^{31}P, {}^{31}P)$ nor librational motion is significant in 5. This is surprisingly in contrast to the conclusion of Tutunjian and Waugh (44). Based on a single-crystal NMR experiment, Tutunjian and Waugh (44) claimed that ${}^{1}J({}^{31}P, {}^{31}P)$ in 5 is significantly anisotropic, $\Delta^{1}J({}^{31}P, {}^{31}P) = 2.3$ kHz. The reason for this discrepancy is still not clear. It is worth mentioning that an NMR experiment was also carried out at -100 °C for the static powder sample of 5 and the spectrum showed essentially no difference compared with that obtained at the room temperature, 22°C. This implies that the librational motion in 5 is insignificant at room temperature.

Once R_{eff} is determined, possible orientations of the chemical shift tensor can be readily calculated from Eq.(3.14). The principal components of the phosphorus chemical shift tensors were determined: $\delta_{11} = 108$, $\delta_{22} = 100$ and $\delta_{33} = -55$ ppm. Because of the lack of molecular symmetry in 5, two sets of orientations are possible: (1) $\phi_{11} = 56^{\circ}$, $\phi_{22} = 64^{\circ}$, $\phi_{33} = 45^{\circ}$ and (2) $\phi_{11} = 53^{\circ}$, $\phi_{22} = 47^{\circ}$, $\phi_{33} = 66^{\circ}$. Obviously, the two orientations are related by a 180° rotation about the magic orientation; both orientations are quite close (within 7°) to the magic orientation. However, it is noted that the second set of orientation angles yields an angle of 5° between δ_{33} and the P=S bond, which, as far as the phosphorus chemical shift tensor is concerned, is in agreement with the singlecrystal NMR result of Tutunjian and Waugh (44,45).

As already mentioned, there is a disagreement between the results presented here and the work of Tutunjian and Waugh (44) on the anisotropy of ${}^{1}J({}^{31}P,{}^{31}P)$ in 5. At this stage, no definite conclusion can be reached. In order to solve this problem, single crystal ³¹P NMR studies are under way in this laboratory.

3.4 NMR spectra of AX spin systems

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As has been briefly mentioned in §3.2, when the chemical shift difference of two spins is always much greater than the dipolar coupling between them at all crystallite orientations, the two-spin system is defined as an AX spin system. Similar to A_2 spin systems, the four NMR resonances given by Eqs.(3.8)-(3.11) have the same intensity. This fact will greatly simplify the analysis of NMR spectra arising from AX spin systems. Here the NMR spectra of several AX spin systems will be studied. The general procedure used to analyze such NMR spectra will be illustrated and the information content of the spectra will be discussed.

3.4.1 Phosphorus chemical shift tensors in a fused *cis*-1,2,3-benzothiaphosphole

In this section, static ³¹P NMR spectra of *cis*-2,10-dimethyl[1,2,3]benzothiadiphospholo[2,3b][1,2,3]benzothiaphosphole (6) will be analyzed in order to determine the orientations of the phosphorus chemical-shift tensors. The objective of this section is to demonstrate a useful strategy of combining MAS and static NMR spectra in analyzing dipolar-chemical shift NMR spectra of AX spin systems.

The "butterfly" arrangement of **6** forces the phosphorus electron lone pairs to adopt an eclipsed conformation (59). Because this conformation is unusual for a molecule containing a P(III)-P(III) single bond, it would be of interest to characterize the chemical shift tensor of each of the two phosphorus centres in **6**, where P12 and P6 (the



IUPAC nomenclature) are renumbered as P1 and P2 for convenience. To date there has been only one dipolar-chemical shift NMR study dealing with ${}^{31}P_{-}{}^{31}P$ spin pairs (35) and a full characterization of the ${}^{31}P$ chemical shift tensor in a compound containing a P(III)-P(III) single bond has not appeared.

It is quite common that the molecule under study possesses a mirror plane, such as the cases discussed in §3.3.1 and §3.3.2. Under this condition, one of the three principal components of the chemical shift tensor must be perpendicular to the molecular mirror plane. In the case of **6**, the "butterfly" molecule has an approximate mirror plane containing the P-P bond. Therefore, the principal component that is perpendicular to the mirror plane must also be perpendicular to the P-P bond. Assuming that this component is ω_{ii} for one nucleus (either A or X), matrix elements of the effective dipolar/chemical shift tensor **T** at this nucleus in the AX spin system (*37,41*) are given by Eqs.(3.16)-(3.20):

$$T_{ii} = \omega_{ii} + 2\pi m (R_{eff} + J_{iso})$$
 (3.16)

$$T_{jj} = \omega_{jj} + 2\pi m \left[R_{eff} \left(1 - 3\cos^2 \phi_{jj} \right) + J_{iso} \right]$$
(3.17)

$$T_{kk} = \omega_{kk} + 2\pi m \left[R_{eff} \left(1 - 3\sin^2 \phi_{jj} \right) + J_{iso} \right]$$
(3.18)

$$T_{jk} = T_{kj} = -3\pi m R_{eff} \sin 2\phi_{jj}$$
(3.19)

$$T_{ij} = T_{ji} = T_{ik} = T_{ki} = 0 aga{3.20}$$

where *i*, *j*, k = 1, 2, 3, and cyclic permutations, ϕ_{jj} is the angle between ω_{jj} of the chemical shift tensor and the dipolar vector, and $m = +\frac{1}{2}$ or $-\frac{1}{2}$, corresponding to the two dipolar subspectra.

The matrix of Eqs.(3.16)-(3.20) can be diagonalized and the three principal values of each subspectrum are given by Eqs.(3.21)-(3.23):

$$T_i = \omega_{ii} + 2\pi m (R_{eff} + J_{iso})$$
 (3.21)

$$T_{j} = \frac{1}{2} \left[\omega_{jj} + \omega_{kk} + 2\pi m \left(2J_{iso} - R_{eff} \right) + \alpha \right]$$
(3.22)

$$T_{k} = \frac{1}{2} \left[\omega_{jj} + \omega_{kk} + 2\pi m \left(2J_{iso} - R_{eff} \right) - \alpha \right]$$
(3.23)

where

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$$\alpha = [(\omega_{jj} - \omega_{kk})^2 - 12\pi m(\omega_{jj} - \omega_{kk})R_{eff}\cos 2\phi_{jj} + 36\pi^2 m^2 R_{eff}^2]^{1/2} \quad (3.24)$$

When $|\omega_{jj} - \omega_{kk}| \ge 2\pi R_{eff}$, one can neglect the off-diagonal elements in Eqs.(3.16)-(3.20) and obtain the three principal values of the effective dipolar/chemical shift tensor T to the zeroth-order approximation:

$$T_i = \omega_{ii} + 2\pi m \left(R_{eff} + J_{iso} \right)$$
(3.25)

$$T_{j} - \omega_{jj} + 2\pi m \left[R_{eff} \left(1 - 3\cos^{2}\phi_{jj} \right) + J_{iso} \right]$$
(3.26)

$$T_{k} - \omega_{kk} + 2\pi m \left[R_{eff} \left(1 - 3\sin^{2}\phi_{jj} \right) + J_{iso} \right]$$
(3.27)

It is readily seen from Eqs.(3.25)-(3.27) that the isotropic positions of the dipolar subspectra for each nucleus occur at $\omega_{iso} \pm \pi J_{iso}$, respectively. Therefore, two *J*-coupled doublets will be observed for a homonuclear AX spin pair under the MAS condition. Based on the intensity distribution of the spinning sidebands, two effective dipolar/chemical shift tensors can be recovered for each nucleus, from which the effective dipolar coupling constant and the relative orientation of the chemical shift tensors in the molecular frame can be deduced. For AX spin systems, the difference between effective tensor components at the direction perpendicular to the dipolar vector gives direct information on the effective dipolar coupling constant, since $\Delta T_i = T_i^+ - T_i^- = 2\pi (R_{eff} + J_{iso})$. The positive and negative superscripts refer to the sign of the spin-

Analysis of MAS spectra. The slow MAS ³¹P NMR spectrum of **6** with a spinning frequency of 4.0 kHz is shown in Fig.3.11. Two isotropic doublets were found centred at 75.8 and 52.0 ppm, respectively, and were assigned to the two phosphorus nuclei in **6**. The observation of a single peak for each phosphorus site in **6** is consistent with the X-ray structure which indicates the triclinic unit cell contains two crystallographically equivalent molecules (59). Both of these isotropic chemical shifts appear at lower frequencies than those observed in solution, *i.e.*, 88.3 and 65.4 ppm for P1 and P2

respectively (59). The large number of spinning sidebands associated with each isotropic



Figure 3.11 The ³¹P CP/MAS NMR spectrum of a fused *cis*-1,2,3-benzothiaphosphole,
 6, at 4.70 T. The sample spinning frequency was 4.0 kHz. The isotropic peaks are indicated by the arrows.

doublet in the MAS spectrum shown in Fig.3.11 indicates that the chemical shift anisotropies at both phosphorus sites are large. The splitting of each doublet was 160 \pm 5 Hz, arising from ¹J(³¹P, ³¹P), and was confirmed by obtaining MAS spectra at a higher field strength (B_o = 9.40 T). This splitting was independent of the sample spinning frequency at both fields, 4.70 and 9.40 T. Although the homonuclear dipolar interaction between the two adjacent phosphorus nuclei is large in this compound (ca.

 $R_{DD} = 1770$ Hz based upon the P-P bond length, $r_{PP} = 2.234$ Å, determined by X-ray diffraction), no spinning-frequency dependent splitting was observed as previously reported in the ³¹P NMR spectra of dipolar coupled phosphorus spin pairs in some inorganic phosphates which contain ³¹P nuclei with identical isotropic chemical shifts (60,61). Here, the large isotropic chemical shift difference between the two ³¹P nuclei in **6** is responsible for this observation. A detailed discussion of spinning-frequency dependent MAS NMR spectra will be the subject of Chapter 4.

The magnitude of ${}^{1}J({}^{31}P, {}^{31}P)$ in **6** is substantially smaller than the typical values reported for compounds containing two directly bonded tricoordinate phosphorus atoms, but significantly larger than those involving two five-coordinate phosphorus atoms (62,63). Interestingly, ${}^{1}J({}^{(31}P, {}^{31}P)$ for **6** in the solid state is also significantly smaller than the value observed in solution, 211.5 Hz (59). Since ${}^{1}J({}^{(31}P, {}^{(31}P))$ is very dependent on the local geometry at the P-P unit, the observation of a smaller J in the solid state may indicate a slightly different geometric structure due to crystal packing effects. Such a change in conformation may also explain the rather large difference in solution and solid state isotropic chemical shifts (≈ 12 ppm). It is worth noting that a correlation between the value of ${}^{1}J({}^{(31}P, {}^{(31}P))$ and the ${}^{(31}P$ chemical shift in solution was reported for various tetraalkyldiphosphanes with different alkyl groups (64). The observed changes of ${}^{1}J({}^{(31}P, {}^{(31}P))$ and $\delta({}^{(31}P)$ in **6**, on going from the solution state to the solid state, follow the same trend, which may indicate that the crystal packing effect somewhat forces the two "wings" of the butterfly molecule **6** to open slightly wider in crystals.

As stated previously, for an isolated spin pair the dipolar interaction manifests

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itself in the intensity distribution of each individual J-coupled sideband pattern. In Fig.3.11 the spinning sidebands associated with the two isotropic doublets correspond to four different powder patterns, which are the four subspectra of a homonuclear spin pair. From the relative intensity of these spinning sidebands, all 12 principal components of the four effective dipolar-chemical shift tensors are readily calculated using the procedure of Herzfeld and Berger (65) and the results are summarized in Table 3.3. The differences between corresponding principal components due to two relevant subspectra at each ³¹P nucleus, $\Delta T_i = T_i^+ - T_i^-$ (*i*=1, 2, 3), are also given in Table 3.3.

Phosphorus ^b	T ₁	T ₂	T ₃	ΔT_1	ΔT_2	ΔT_3
P1(+) P1(-)	119 134	119 130	-7 -40	-15	-11	+33
P2(+) P2(-)	207 178	17 33	-66 -58	+29	-16	-8

Table 3.3 Principal values^a of the effective dipolar-chemical shift tensor in **6**

^{*a*}The tensor components are in ppm and errors are estimated to be ± 2 ppm. ^{*b*}The plus and minus signs describe the high and low frequency peaks in each Jcoupled doublet, respectively.

From the results shown in Table 3.3, the span of the dipolar subspectrum, defined as $|T_1 - T_3|$, is larger for the low-frequency peak of the P1 doublet than for the highfrequency one. This indicates that the absolute sign of the J coupling constant is negative (41). The spans of the dipolar subspectra for the P2 doublet are in an opposite order, since the anisotropy is *negative* at P2, *i.e.*, $|T_1 - T_{iso}| > |T_3 - T_{iso}|$, again confirming a negative ${}^{1}J({}^{31}P, {}^{31}P)$. This is in agreement with the general observations and theoretical calculations of the sign of ${}^{1}J({}^{31}P, {}^{31}P)$ couplings (63).

The crystal structure of compound **6** indicates that, to a good approximation, the molecule has a mirror plane containing the P-P bond. As will be shown later, the excellent agreement between the observed powder lineshapes and the calculated spectra supports this assumption. This element of molecular pseudo-symmetry requires that one of the principal axes for each of the ³¹P chemical shift tensors be perpendicular to the mirror plane, and therefore perpendicular to the dipolar vector. Therefore, only one angle is required to specify the other two principal axes in the approximate mirror plane.

Given that the four subspectra contain a total of 12 effective principal components, one has enough information to solve all ten remaining unknowns in this system: they are the six principal components for the two phosphorus chemical shift tensors, one isotropic J coupling constant, one effective dipolar coupling constant and two angles which specify the orientation of the dipolar vector in the principal axis system of the two phosphorus chemical shift tensors.

As mentioned previously, the difference between the effective tensor components along the direction perpendicular to the dipolar vector gives directly the sum of the effective dipolar coupling constant and the isotropic J coupling constant. From the data given in Table 3.3 one readily obtains that δ_{11} of P1 and δ_{22} of P2 are perpendicular to the molecular mirror plane respectively and that the effective dipolar coupling constant is $R_{eff} = 1.4 \pm 0.2$ kHz. Substituting the T_i (i=1, 2, 3) values listed in Table 3.3 and R_{eff} into Eqs.(3.25)-(3.27), the chemical shift tensor components and their orientations were obtained. Calculations yield the following principal components for the phosphorus chemical shift tensors: at P1, $\delta_{11} = 127$, $\delta_{22} = 124$, $\delta_{33} = -24$ ppm and at P2, $\delta_{11} = 192$, $\delta_{22} = 25$, $\delta_{33} = -62$ ppm. The standard errors on these values were estimated to be ± 2 ppm. Also, the calculations indicate that the angle between δ_{22} of P1 and the dipolar vector is $72 \pm 5^{\circ}$ while the angle between δ_{33} of P2 and the dipolar vector is 67 $\pm 5^{\circ}$. Eqs.(3.21)-(3.23) were also used for the above calculation and nearly identical results were obtained within experimental error, indicating that the condition of $|\omega_{jj} - \omega_{kk}| \ge 2\pi R_{eff}$ is valid in the present case, where ω_{jj} and ω_{kk} describe the two principal components in the pseudo-mirror plane.

Analysis of the static spectra. The static ³¹P NMR spectrum of **6** is shown in Fig.3.12. In order to examine the validity of the above calculations, *i.e.*, to test the assumption that the ³¹P spin pair in **6** can be treated as a homonuclear AX spin system, complete lineshape simulations were carried out using the exact expressions given by Eqs.(3.8)-(3.11). Although it is difficult to infer second-order (AB) character from spinning sidebands, it should be readily apparent from static NMR lineshapes. The results from the analysis of the slow MAS spectrum were used as initial inputs for the simulation and were further refined by comparing the observed powder lineshape with the simulated spectrum. The final best-fit parameters for the two phosphorus chemical shift tensors are given in Table 3.4. The effective dipolar coupling constant was adjusted to be $R_{eff} = 1.6 \pm 0.1$ kHz. This observed dipolar coupling constant is somewhat smaller than expected from the X-ray bond-length consideration, $R_{DD} = 1770$ Hz. There are two possible reasons for such a decrease in the effective dipolar coupling constant. First, motional averaging may reduce the dipolar coupling constant. Second, there may be anisotropy in the indirect spin-spin interaction, ΔJ (see Eq.(2.27)). Theoretical *ab initio* calculations of ${}^{1}J({}^{31}P,{}^{31}P)$ in P₂H₄ indicated that the Fermi contact mechanism is predominant for the cis conformation (*66,67*). Since the Fermi contact mechanism is isotropic, ΔJ is expected to be small in **6**. Therefore, the deviation of R_{eff} from R_{DD} is probably due to motional averaging.

Phosphorus	$\delta_{ m iso}$	δ ₁₁	δ ₂₂	δ ₃₃	Ω	κ	φ ₃₃
P1	75.8	129	122	-25	154	0.90	10°
P2	52.0	190	25	-54	244	-0.33	80°

Table 3.4Principal components^a and orientations of ${}^{31}P$ chemical shift
tensors in 6

^{*a*}All chemical shifts are in ppm and estimated errors are ± 2 ppm.

It was found that the static NMR lineshape simulations were more sensitive to the orientation of the chemical shift tensors than to the magnitude of the principal components. As a result, all principal components in Table 3.4 are essentially the same as those obtained from the analysis of the slow MAS spectrum (except for δ_{33} of P2) while the orientations of the two chemical shift tensors are modified by approximately 10° .



Figure 3.12 (A) Experimental static ³¹P NMR spectrum of a fused cis-1,2,3-benzothiaphosphole, 6; (B) Calculated static ³¹P NMR spectrum of 6 using the parameters in Table 3.4; (C) and (D) Calculated dipolar subspectra for P1 and P2, respectively, using the same parameters as in (B).

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In a general heteronuclear AX spin system, any rotation of the chemical shift tensors about the dipolar vector will give invariant NMR lineshapes in the static experiment or intensity distribution of spinning sidebands in the slow MAS experiment. However, for a homonuclear spin pair, one has to be cautious of such a statement, since the relative orientation of the two chemical shift tensors with respect to one another may become important. As will be shown in §3.5, two chemical shift tensors are fixed in an AB spin pair to give a unique NMR lineshape. Even in the homonuclear AX approximation, it is still possible that changing the relative orientation between the two chemical shift tensors may break down the validity of the AX approximation, at least in some directions. Within the constraints of the molecular symmetry, the number of possible orientations has been reduced to two for each phosphorus chemical shift tensor. Given that the angles between δ_{33} of the two chemical shift tensors (ϕ_{33} in Table 3.4) and the dipolar vector are known, there are still four possible ways to orient two chemical shift tensors in the molecule, since both angles could be either positive or negative. All four possible orientations were put into the lineshape simulation program and a best fit is portrayed in Fig.3.12. A schematic diagram illustrating the orientations of two phosphorus chemical shift tensors determined through this work is presented in Fig.3.13. It places δ_{33} of P1 10° away from the internuclear vector towards the electron lone pair at P1, with δ_{22} lying almost in the S-P1-S plane. The determination of the chemical shift tensor at P2 requires that δ_{33} lie in the mirror plane, being rotated by 80° from the P-P bond as indicated in Fig.3.13. Similarly, δ_{33} of P2 is nearly in the plane containing the C-P2-C fragment. Simulated dipolar subspectra of each ³¹P nucleus are also shown

in Fig.3.12 using the same parameters given in Table 3.4. The sum of the four subspectra for P1 and P2 gives the total NMR lineshape shown in Fig.3.12. One does not observe any AB character in these calculated dipolar subspectra indicating that two ³¹P nuclei in **6** could be treated as an AX spin system at $B_0 = 4.70$ T. One might at first expect some AB character for the ³¹P-³¹P spin pair in **6**, since the difference between the isotropic chemical shifts of P1 and P2, 24 ppm (ca.1944 Hz at $B_0 = 4.70$ T), is comparable to the dipolar coupling constant between them, $R_{DD} = 1770$ Hz. However, one should realize that the ratio between the isotropic chemical shift difference and R_{DD} is not the correct criterion for judging whether a dipolar-coupled spin pair should be analyzed as an A₂, AB or AX spin system. Because of the tensorial nature of



Figure 3.13 A schematic diagram of the orientation of the two ³¹P chemical shift tensors in **6** obtained from an analysis of the ³¹P NMR spectrum of a static powder sample. $\delta_{11}(P1)$ and $\delta_{22}(P2)$ are perpendicular to the approximate mirror plane of the molecule.

chemical shifts in solids, one has to consider the relative orientation of the two chemical shift tensors which make up the two-spin system. Although there is extensive overlap of the four dipolar subspectra in 6, it was found that, at almost all orientations of \mathbf{r}_{PP} with respect to the applied magnetic field, the AX approximation is valid. For example, if the magnetic field lies perpendicular to the molecular mirror plane, an orientation in which δ_{11} of P1 and δ_{22} of P2 are coincident, the chemical shift difference is about 100 ppm (ca. 8100 Hz at $B_0 = 4.70$ T). This is much greater than the dipolar coupling at this orientation, 800 Hz. A similar discussion also applies for the two orthogonal orientations. Extensive computer calculations of the ratio, $\omega_D / [\omega(P1)-\omega(P2)]$, as a function of orientation indicate that this ratio is always less than 0.1 except when the polar angle is approximately 50° and the azimuthal angles are 50°-60° and 300°-310°. The actual contributions that these latter orientations make to the over-all lineshape are negligible.

Since the relative positions of the 12 principal components in the four dipolar subspectra are dependent on the applied magnetic field, it would be of interest to examine the NMR lineshape at a different field. Hence, an experiment was carried out at a higher field, 9.40 T. It is readily seen from Fig.3.14 that, at 9.40 T, singularities at the low frequency region of the NMR line shape become more visible than those in the low-field spectrum. Using parameters listed in Table 3.4, the simulated NMR lineshape is also shown in Fig.3.14. The good agreement between the observed and simulated NMR lineshapes provides further evidence that the AX approximation is valid in the present case.

The possible orientations of δ_{33} where two ϕ_{33} 's have different signs have been ruled out, since they result i:, an inferior fit. An alternative assignment occurs if both chemical shift tensors are rotated simultaneously about the dipolar vector by 180°, giving



Figure 3.14 Observed (top) and simulated (bottom) 31 F static NMR spectrum for the fused *cis*-1,2,3-benzothiaphosphole, **6**, at 9.40 T.

two negative ϕ_{33} 's. Although this gives an identical static NMR lineshape, it will be argued below that the assignment shown in Fig.3.13 is more reasonable.

The chemical shift tensor of P1 shows near axial symmetry ($\delta_{11} \approx \delta_{22}$), although there is no apparent local symmetry in the molecular structure that would imply an axial symmetry in the chemical shift tensor. Since it has been determined that δ_{11} of P1 is perpendicular to the molecular mirror plane, it is also perpendicular to the electron lone Sum 1 62

pair at P1. If one places δ_{33} of P1 10° away from the dipolar vector in the direction opposite to that shown in Fig.3.13 (*i.e.*, $\phi_{33} = -10^\circ$), the direction of δ_{22} would lie nearly along the electron lone pair. Since it seems unlikely that the chemical shielding would be the same along the lone pair (δ_{22} component) as in the direction perpendicular to the lone pair (δ_{11} component), this alternative assignment is discounted.

The results in Table 3.4 indicate that the span of the phosphorus chemical shift tensor of P2, $\Omega = 244$ ppm, is much larger than the values reported in two related compounds containing a P-P single bond (35,61) and by a theoretical calculation on P_2H_4 (68). The phosphorus chemical shift anisotropy in tetraphenyldiphosphine was also found to be relatively small ($\Omega = 46$ ppm) (69). Another class of related compounds containing P(III) atoms are phosphines. Still, Ω of P2 appears noticeably large compared with most of the reported values for the phosphines (ca. $\Omega = 6-85$ ppm)(70). Additionally, the isotropic chemical shift of P2 in compound $\mathbf{6}$ is at a much lower field than the above mentioned phosphines and diphosphines. The large chemical shift anisotropy and large isotropic shift at P2 in 6 result primarily from the significant deshielding in the δ_{11} and δ_{22} directions, which approximately define a plane normal to the P-P bond. Probably, the unusual cis conformation of the adjacent electron lone pairs in **6** is responsible for the relatively large chemical shift anisotropy at P2. However, given the complicated nature of chemical shifts and lack of reliable theoretical calculations, phosphorus chemical shift tensors are far from being fully understood.

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With P1 bonded to two sulphur atoms and one phosphorus atom, its chemical shift anisotropy, $\Omega = 154$ ppm, falls in the normal range reported for related compounds containing P-S single bonds. Clearly, a complete understanding of the ³¹P chemical shift anisotropy still requires far more work from both experimentalists and theoreticians.

In summary, it has been demonstrated that the dipolar-chemical shift NMR method is a valuable alternative to single crystal NMR in providing a full characterization of the ³¹P chemical shift tensor in **6**. It is advantageous to combine the MAS experiment with the non-spinning experiment in dealing with a dipolar-coupled ³¹P spin pair when there is a resolvable *J* coupling between the two nuclei. The resolved *J*-coupled sideband patterns in the MAS spectrum make it possible to separate different dipolar subspectra and to provide a good starting point for interpreting the static NMR lineshape. The static NMR lineshape contains all the information on the dipolar interaction and the chemical shift tensors, and thus serves as a test for the AX approximation which is generally used for analyzing dipolar subspectra in MAS experiments.

3.4.2 Carboxyl carbon chemical shift tensors in phenylacetic acid and potassium phenylacetate

Most of the previously characterized carbon chemical shift tensors are derived from single-crystal NMR studies (71). Since the early work by Grant and co-workers (37,38), in which they introduced the dipolar-chemical shift NMR method in studying small, matrix-isolated molecules, there has been no report in the literature using the ¹³C dipolar-chemical shift NMR method to study ¹³C-¹³C spin pairs in polycrystalline solids. In §3.3.2 one has seen that carbon chemical shift tensors are characterized in or₁₅anic and organometallic compounds by using the dipolar-chemical shift NMR method under the A_2 approximation. In this section, carbon chemical shift tensors in other two types of organic compounds, carboxylic acids and carboxylates, will be investigated. More specifically, carboxyl carbon chemical shift tensors will be studied using two model compounds, phenylacetic acid-1,2-¹³C₂ (7) and potassium phenylacetate-1,2-¹³C₂ (8). Since the chemical shift of a methylene carbon is remarkably different from that of a carboxyl carbon, the spin systems in 7 and 8 can be treated as AX spin systems.

The static ¹³C NMR spectra of 7 and 8 are shown in Fig.3.15. Clearly, each of the two spectra consists of four dipolar subspectra. The most striking feature in Fig.3.15 is that, on going from 7 to 8, the spectral region for the carboxyl carbon changes dramatically, whereas the methylene carbon region appears almost unchanged. Since ${}^{1}J({}^{13}C, {}^{13}C)$ is too small to be resolved in ${}^{13}C$ MAS NMR spectra of both compounds, the procedure of §3.4.1 is not applicable. Therefore, a procedure based on complete lineshape simulation must be employed. It is generally helpful to estimate first the principal components of the chemical shielding tensor and then to determine the tensor orientation. Since in the spectra of both 7 and 8 two spectral regions arising from methylene and carboxyl carbons respectively are separated from one another, one can calculate the orientation of each of the two chemical shift tensors individually.

The crystal structure of 7 has been determined by a recent X-ray diffraction study (72). The molecule of 7 possesses an approximate mirror plane containing C(1p)-C(2)-C(1) and two oxygen atoms. Therefore, one of the principal components must be perpendicular to the mirror plane as well as the C(2)-C(1) bond. Previous experimental and theoretical results of carbon chemical shift tensors have shown that the most shielded



Figure 3.15 Observed and calculated ¹³C static NMR spectra of (top) phenylacetic acid-1,2-¹³C₂, 7, and (bottom) potassium phenylacetate-1,2-¹³C₂, 8, at 4.70 T. Top: number of transients, 6367; recycle time, 10s. Bottom: number of transients, 128; recycle time, 128.

component, δ_{33} , of the carbon chemical shift tensor in the C=X (X = C, O, N, S) fragment is always nearly perpendicular to the C=X plane (71, 73-75). This is also clear in the static ¹³C NMR spectra of 7 and 8 where the splitting at the δ_{33} component is 1.98 and 1.96 kHz for 7 and 8, respectively, in reasonable agreement with $R_{DD} \approx 2.2$ kHz. Complete lineshape simulations yield the orientations of the carbon chemical shift tensors for the carboxyl carbons. For compound 7, δ_{11} of the carboxyl carbon makes an angle of 43° with the ¹³C-¹³C bond while a significantly smaller angle, 5°, was obtained for compound 8. Although the symmetry argument is also valid in the determination of the carbon chemical shift tensors of the methy lene carbons, the process is, however, less straightforward. It was found that the δ_{11} component of the methylene carbon chemical shift tensor is perpendicular to the molecular mirror plane. The principal components are summarized in Table 3.5 and the orientations are depicted in Fig.3.16.

Carbon	$\delta_{ m iso}$	δ ₁₁	δ ₂₂	δ ₃₃	Ω	к
methylene (7)	41	55	51	17	38	0.79
methylene (8)	46	63	58	18	45	0.80
carboxyl (7)	181	257	176	110	147	-0.10
carboxyl (8)	179	242	185	111	131	0.14

Table 3.5 Carbon chemical shift tensors^a in phenylacetic acid-1,2⁻¹³C₂ (7) and potassium phenylacetate-1,2⁻¹³C₂ (8).

^aAll carbon chemical shifts are in ppm.

Since the ¹³C spin-pair systems in 7 and 8 are AX spin systems, each of the carbon chemical tensors shown in Fig.3.16 suffers a two-fold ambiguity. By comparing the possible solutions with the results from *ab initio* shielding calculations (76), one is able to solve these ambiguities, except for the chemical shift tensor of the methylene carbon in 8 since the crystal structure of 8 is not available.



Figure 3.16 Orientations of the carbon chemical shift tensors in (top) phenylacetic acid-1,2⁻¹³C₂, 7, and (bottom) potassium phenylacetate-1,2⁻¹³C₂, 8.

The orientations of the carbon chemical shift tensors found in 7 and 8 are in excellent agreement with the previous results on related carboxylic acids and carboxylates by single-crystal NMR studies (71). This indicates that dipolar-chemical shift NMR is

a useful and reliable method in determining chemical shift tensors. Most of the previous single-crystal NMR studies of carboxyl tensor orientation in either carboxylic acids or carboxylates are limited only to small molecules containing less than three different carbons. This is clearly due to the fact that, as the size of an organic molecule is increased, the number of peaks in ¹³C NMR specua becomes increasingly large, hence, the single-crystal ¹³C NMR spectra are difficult to analyze. However, it is noted that, with the combination of a specially-designed single-crystal probe and more advanced multi-dimensional NMR techniques, Grant and co-workers (77) have recently demonstrated that an analysis of ¹³C single-crystal NMR spectra becomes practical for complex molecules such as sugars. Even though, it is anticipated that the dipolar-chemical shift NMR method will still be useful in characterizing carbon chemical shift tensors, especially when one is interested only in specific carbons.

3.5 NMR spectra of AB spin systems

In §3.3 and §3.4, static NMR spectra arising from two special types of homonuclear spin-pair systems, A_2 and AX, have been investigated. One common feature in all those static NMR spectra is that the dipolar subspectra can be characterized using a single mathematical function but different parameters. This mathematical function is identical to that for a chemical-shift powder pattern, hence, it requires only three parameters to be defined (37,41). In other words, each of the dipolar subspectra can be visualized as a lineshape arising from an effective dipolar-chemical shift tensor. Clearly, this common feature is brought about due to the fact that, for any crystallite

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orientation in the applied magnetic field, all the NMR transitions (two for A_2 and four for AX) have identical intensity under the A_2 or AX approximations; see Eqs.(3.8)-(3.11). For a spin-pair system, if there exist some crystallite orientations such that the chemical shift difference of the two spins is comparable to or even smaller than the dipolar coupling between them, the spin system cannot be treated as an AX spin system. This type of spin-pair system is referred to as a second-order spin system or an AB spin system. For an AB spin system, the four NMR transitions will generally have different intensities and the relative intensity distribution of the four transitions will depend on the crystallite orientation as predicted by Eqs.(3.8)-(3.11). This phenomenon has been nicely demonstrated by Griffin and co-workers (78) in single-crystal NMR spectra of diammonium oxlate-¹³C₂. For a polycrystalline sample, the orientation-dependent NMR transitions will complicate the appearance of all dipolar subspectra, resulting in NMR lineshapes which have distinct features compared with chemical-shift powder lineshapes. These distinct features are termed as second-order, or AB, features.

In an early paper, Zilm and Grant (37) first considered AB features in static NMR spectra of polycrystalline solids. However, their low-field experimental spectrum for 1,2-acetaldehyde- ${}^{13}C_2$, where some AB features may be expected, suffered from low sensitivity, hence, no clear AB features were detected. Since then, no study reporting the second-order features in static NMR spectra has appeared in the literature.

The objective of the study outlined in this section is to provide the first examples that clearly illustrate distinct AB features in NMR spectra arising from homonuclear twospin systems in static solids. It will be shown that, as an extension of the dipolarchemical shift NMR method for A_2 and AX spin systems, the relative orientation of the two chemical shift tensors can also be obtained from an analysis of static NMR spectra of AB spin systems.

3.5.1 Nitrogen chemical shift tensors in *cis*-azobenzene and *cis*-azobenzene dioxide

Although nitrogen chemical shift tensors have been studied in numerous compounds, the number of studies concerning the tensorial *orientation* is surprisingly small. To date there have been only three single-crystal NMR studies on nitrogen chemical shift tensors (79-81). Other orientation determinations of nitrogen chemical shift tensors are based on the dipolar-chemical shift NMR method, mostly involving heteronuclear spin pairs. One classic example of NMR studies of homonuclear ¹⁵N-¹⁵N spin pairs is the study of solid nitrogen at 4.2 K by Ishol and Scott (82). The only other NMR study of ¹⁵N spin pairs is a recent report by Wasylishen *et al.* (39), in which they obtained the nitrogen chemical shift tensors in *trans*-azobenzene-¹⁵N₂. In both cases, however, the ¹⁵N spin pairs are A₂ spin systems.

It is known that the solution state ¹⁵N chemical shift of *cis*-azobenzene is about 220 ppm more deshielded than that of *cis*-azobenzene dioxide (83,84). Clearly, this indicates dramatic differences in the electronic framework of these two compounds, and it was speculated that the deshielding in the *cis*-azobenzene may be due to low-lying $n_N \rightarrow \pi^*$ circulations which enhance the paramagnetic shielding term. Unfortunately, the study of isotropic chemical shifts provides no definitive evidence on the origin of such a large shielding difference. Given the greater sensitivity of the chemical-shift tensor to the nature of the local bonding environment, it will be of interest to characterize nitrogen chemical shift tensors in *cis*-azobenzene-¹⁵N₂ (9) and *cis*-azobenzene-¹⁵N₂ dioxide (10) by using the dipolar-chemical shift NMR method.



X-ray diffraction results for **9** indicate that crystals obtained from petroleum ether are orthorhombic (space group *Pbcn*) with four equivalent molecules in the unit cell (85). Each molecule is nonplanar with each phenyl ring twisted by 53° about the C_{ipso} -N bond relative to the N=N- C_{ipso} fragment. However, the molecule retains a crystallographic C_2 symmetry axis perpendicular to the N=N bond. Furthermore, the planarity at the central N'=N moiety of **9** is very good with the dihedral angle C1'-N'=N-C1 being only 8°. Therefore, one of the principal components must be approximately perpendicular to the N=N fragment plane and the two nitrogen chemical-shift tensors in **9** are also related by the crystallographic C_2 axis. Similarly, crystals of **10** are also orthorhombic (space group *Pbcn*, Z = 8), but the two nitrogen atoms are slightly non-equivalent (86). In the ¹⁵N CP/MAS spectra of **10**, two peaks were observed at 311.1 and 308.9 ppm. Because of the molecular structure and the small difference in the isotropic ¹⁵N chemical shift, the two nitrogen chemical shift tensors in 10 are assumed to have the same magnitudes. The two nitrogen chemical shift tensors in 10 are then related by an approximate C_2 symmetry axis in the molecular frame.

The static ¹⁵N NMR spectra of 9 and 10 are shown in Fig.3.17. Comparison of the observed NMR lineshapes for 9 and 10 with those previously studied in §3.3 and §3.4 reveals some distinct features in the spectra of the former. Although, at the δ_{33} region, both spectra shown in Fig.3.17 exhibit splittings similar to those found in A_2 and AX spin systems, drastically different spectral features are observed in the δ_{11} - δ_{22} regions. For example, it can be seen very clearly in the spectrum of 9 that there are *three* distinct shoulders at the δ_{11} end of the spectrum. As noted earlier, for either an A_2 or an AX spin pair there would be only *two* such shoulders at the δ_{11} region. Apparently, the new shoulder immediately indicates that the ¹⁵N spin pair in 9 cannot be treated as either an A₂ or an AX spin system. In addition, there is a small peak to high-frequency of the two large peaks in the δ_{22} region. Again, this extra peak results from the AB character of the homonuclear spin pair in 9. It is also clearly seen in the spectrum of 10 that two extra peaks appear between the δ_{11} and δ_{22} regions, which are not expected in NMR lineshapes arising from either an A2 or an AX spin system. Therefore, one must treat the spin pairs in 9 and 10 as general AB spin systems.

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The splittings at the δ_{33} regions in the observed spectra shown in Fig.3.17 were measured to be 944 and 785 Hz for 9 and 10, respectively. From the crystal structures of the two compounds, the direct dipolar couplings between the two ¹⁵N nuclei in 9 and

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Figure 3.17 Nitrogen-15 static NMR spectra of (top) cis-azobenzene-¹⁵N₂, **9**, and (bottom) cis-azobenzene-¹⁵N₂ dioxide, **10**, at 4.70 T. Top: number of transients, 2244; recycle time 60 s. Bottom: number of transients, 4075; recycle time, 60 s.

10 are 528 and 540 Hz, respectively. As has been mentioned in §3.3, the splittings can be explained as arising from A₂ spin systems in which the δ_{33} components are perpendicular to the dipolar vector, *i.e.*, the N=N bond. Because of the arguments stated earlier in this section, it is clear that, whichever component is perpendicular to the N=N fragment, the spin system can be described exactly as an A₂ system when the applied magnetic field lies along this component. Therefore, without going into any lineshape simulation, one is able to reach the conclusion that the δ_{33} components in both 9 and 10 must be oriented perpendicular to the N=N fragment plane.

Based on Eqs. (3.8)-(3.11), simulations of the complete lineshapes yield the two nitrogen chemical shift tensors in **9** and **10** and the calculated spectra are also shown in Fig. 3.17. The results of the principal components are listed in Table 3.6 and the orientations of the chemical shift tensors are depicted in Fig. 3.18. The orientations of

Compound	$\delta_{ m iso}^{~~b}$	δ ₁₁	δ ₂₂	δ ₃₃	Ω	К,
9 10	528.8 311.1 308.9	1006 465	469 288	112 180	894 285	-0.20 -0.24

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Table 3.6 Nitrogen chemical shift tensors^a in *cis*-azobenzene (9) and *cis*-azobenzene dioxide (10).

^aAll principal components are in ppm and estimated errors are \pm 2 ppm; ^bObtained from MAS NMR spectra. the δ_{33} components were confirmed in both 9 and 10. The δ_{11} component was found to make an angle of 15° and 23° to the N=N bond in 9 and 10, respectively. In principle, the dipolar-chemical shift method always leaves a two-fold ambiguity because the static NMR lineshape is invariant to a simultaneous 180° rotation of the two chemical shift tensors about the N=N bond. In practice, this ambiguity can be solved by considering the results from *ab initio* shielding calculations. The *ab initio* shielding calculations of the nitrogen chemical shift tensors of *cis*-diazene (55) and *cis*-diazene dioxide (30) suggest that the orientations depicted in Fig.3.18 are reasonable descriptions of the shielding environments in 9 and 10.



Figure 3.18 The orientations of the nitrogen chemical shift tensors in (top) *cis*azobenzene (9) and (bottom) *cis*-azobenzene dioxide (10).

From Table 3.6 it is clearly seen that the span of the nitrogen chemical shift tensor in 9 is three time greater than that in 10. More interestingly, the large chemical shift anisotropy in 9 results mainly from the fact that the δ_{11} component is remarkably deshielded compared with the principal components in 10. Obviously, since the δ_{11} component is oriented perpendicular to both the π electron manifold and the location of the electron lone pair at the nitrogen, the chemical shielding along this direction will be correlated to the $n_N \rightarrow \pi^*$ transition, which is low lying in energy due to the nonbonding nature of the nitrogen lone pair electrons. This results in a large paramagnetic shielding along the δ_{11} direction. In the case of 10, however, the nitrogen lone-pair electrons become involved in bond formation, decreasing the paramagnetic shielding for axes in the N=N fragment plane. In both 9 and 10, the most shielded component (δ_{33}) is perpendicular to the N=N fragment plane and is a result of high energy $\sigma \rightarrow \sigma^*$ circulations. Notice that the magnitudes of the most shielded components are very similar. These findings are consistent with previous experimental and theoretical results on other molecular fragments containing dicoordinate nitrogen involved in double bonds (39,75,87,88).

It is interesting to examine how the AB features in the ¹⁵N NMR spectrum depend on the relative orientation of the two chemical shift tensors. Consider the case of **9** as an example. Calculated static NMR spectra of **9** as a function of the angle (γ^{CS}) between the δ_{11} component and the N=N bond are shown in Fig.3.19. It is clear that the AB features present in the static NMR spectra are very sensitive to the relative orientation between the two chemical shift tensors. When $\gamma^{CS} = 0^{\circ}$ or 90°, the two nitrogen



Figure 3.19 Calculated static NMR spectra showing the variation of the AB feature at the δ_{11} and δ_{22} regions as a function of the angle γ^{CS} .

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chemical shift tensors become coincident, leading to an A₂ spin system. In Fig.3.19, at these two angles, the static NMR spectra exhibit smooth lineshapes, each consisting of two chemical shift powder patterns as expected for A₂ spin systems. As long as γ^{CS} deviates from 0° or 90°, the two chemical shift tensors have different orientations, hence, distinct AB features are evident in the δ_{11} - δ_{22} region. Note that the lineshape at δ_{33} is independent of the angle γ^{CS} .

3.5.2 Phosphorus chemical shift tensors in novel trans- and cis-1-phenyl-2-methyl-**3,4-bis**(*tert*-butyl)diphosphetes

Early UV-photoelectron spectroscopy (89) and X-ray crystallography (90,91) studies showed that the electron lone pairs of the phosphorus atoms have a negligible coupling to the C=C π molecular orbital in diphosphete derivatives. However, these studies were focused only on compounds in which the phosphorus electron lone pairs adopt a trans conformation. Recently, Mathey and co-workers (92) successfully synthesized two novel phosphete derivatives: *trans*-1-phenyl-2-methyl-3,4-bis(*tert*-butyl)diphosphete (11) and *cis*-1-phenyl-2-methyl-3,4-bis(*tert*-butyl)diphosphete (12).



Interestingly, the electron lone pairs of the two phosphorus atoms in 11 are trans to one another whereas those in 12 are in a cis arrangement. The X-ray crystal structure analysis shows no evidence for cyclic delocalization in both compounds because the P-C and C=C bond lengths are in the normal range. However, the solution state ³¹P chemical shifts of 11 and 12 appear between -46 and -61 ppm (92), which are more shielded than typical organophosphines. Given the advantage of solid state NMR spectroscopy in characterizing anisotropic chemical shifts, it was of interest to study the phosphorus chemical shift tensors in 11 and 12.

The ³¹P MAS NMR spectra of **11** and **12** showed that both compounds are pure. Each ³¹P MAS NMR spectrum exhibited two sets of spinning sidebands arising from two non-equivalent phosphorus nuclei in the molecule. The ³¹P static NMR spectrum of **11** obtained at 9.40 T is shown in Fig.3.20. The observed static spectrum of **11** looks quite



Figure 3.20 Phosphorus-31 static NMR spectra of *trans*-1-phenyl-2-methyl-3,4-bis(*tert*-butyl)diphosphete, **11**, at 9.40 T. 256 transients; recycle time, 10s.

complex at first sight. Close inspection reveals that, at the δ_{33} region, the spectra exhibit smooth lineshapes and clear splittings, typical for an AX spin pair. However, some apparently "irregular" features, now known as the AB features, are observed in the region between δ_{11} and δ_{22} components. Since the molecule **11** lacks any symmetry element, no assumption can be made about the orientation of the phosphorus chemical shift tensors, hence, a complete lineshape analysis can be performed only by a trial-anderror procedure. In practice, principal components of the two phosphorus chemical shift tensors were estimated first, and then the relative orientation of the two tensors can be obtained by comparing the calculated spectra with the observed ones. The ³¹P static NMR spectrum of **12** obtained at 9.40 T is shown in Fig.3.21. Using a similar procedure, the phosphorus chemical shift tensors in **12** can also be determined. The results for the phosphorus chemical shift tensors in **11** and **12** are listed in Table 3.7.



Figure 3.21 Phosphorus-31 static NMR spectra of *cis*-1-phenyl-2-methyl-3,4-bis(*tert*-butyl)diphosphete, **12**, at 9.40 T. Number of transients, 256; recycle time, 10s.

The orientations of the phosphorus chemical shift tensors are depicted in Fig.3.22. Again, the two-fold ambiguity involved was solved by comparing the experimental results with those from theoretical shielding calculations (76). The ³¹P static NMR spectra of 11 and 12 were also obtained at 4.70 T. Simulations of the observed static spectra at 4.70 T confirmed the results given in Table 3.7 and the tensorial orientations depicted in Fig.3.22.

It was found that the δ_{33} components of the two phosphorus chemical shift tensors in 11 are approximately perpendicular to the ring plane. This is in agreement with previous observations in several three-membered phosphorus heterocyclic compounds (93-95). The δ_{11} components for P-Me and P-Ph in 11, lying in the ring plane, make

Compound	$\delta_{ m iso}{}^{ m b}$	δ ₁₁	δ_{22}	δ_{33}	Ω	к
11 (P-Me)	-56.2	90	-70	-190	280	-0.14
11 (P-Ph)	-59.4	38	-5	-210	248	0.65
12 (P-Me)	-56.3	50	-95	-125	175	-0.65
12 (P-Ph)	-42.0	32	-52	-106	138	-0.22

Table 3.7Phosphorus chemical shift tensors^a in *trans*- and *cis*-1-phenyl-
2-methyl-3,4-bis(*tert*-butyl)diphosphetes, **11** and **12**.

^aAll chemical shifts are in ppm.

^bObtained from MAS NMR spectra.

angles of 44° and 40° with respect to the P-P bond, respectively. However, the two tensorial orientations in 12 are quite different. While for P-Ph it is still the δ_{33} component perpendicular to the ring plane, it was found that the δ_{22} component of P-Me

becomes perpendicular to the ring plane. By examining data available in the literature (93, 96-99), Barra and Robert (94) found a linear relationship between the span of the phosphorus chemical shift tensor and the bond angle defining the strain at the phosphorus atom of interest. The results found for 11 and 12 are in qualitative agreement with their proposal.



Figure 3.22 The orientations of the phosphorus chemical shift tensors in 11 (top) and 12 (bottom).

In Table 3.7, it is interesting to note that the chemical shift anisotropy in the trans compound is considerably larger than that of the cis compound. The large chemical shift anisotropy in the trans compound is mainly due to the considerable shielding along the δ_{33} components. Such a discrepancy in the phosphorus chemical shift anisotropy is unlikely to result from the difference in the geometrical structures of the trans and cis compounds, since the endocyclic bond angles at the phosphorus nuclei in 11 and 12 are essentially identical (11: 75.9° and 76.4° ; 12: 76.2° and 76.9°). The observation may indicate that the orientation of the electron lone pairs of the phosphorus atoms plays an important role in determining the shielding environment in these two compounds.

3.6 Experimental

Both the Lawessen's reagent (1) and the Davy's methyl reagent (2) were obtained from Aldrich Chemical Company, Inc. and used without further purification. The compound of *trans*-stilbene- α , β -¹³C₂ (99.5% ¹³C) (3) was obtained from MSD Isotopes (Montreal, Canada) and used without further purification. Pt(*trans*-stilbene- α , β -¹³C₂)(PPh₃)₂ (4) was kindly prepared by Deven Latimer according to the literature method (*100*). Tetraethyldiphosphine disulfide (5) was obtained from Organometallics, Inc.(East Hampstead, NH). Compound **6** (ca. 100mg) was generously provided by Professor G. Baccolini (*59*). Phenylacetic acid-1,2-¹³C₂ (99% ¹³C labeled) (7) was obtained from Aldrich Chemical Company, Inc. and used without further purification. White crystalline solids of potassium phenylacetate (**8**) were prepared by dissolving 300 mg of **7** into 20 ml H₂O, titrating with 0.1 M KOH (24.20 ml), and evaporating the water with a rotary evaporator. The preparations of **9** and **10** are given in (*55*) and (*30*), respectively.

All static ³¹P NMR spectra were recorded on Bruker MSL-200 ($B_0 = 4.70$ T) and Bruker AMX-400 ($B_0 = 9.40$ T) NMR spectrometers operating for ³¹P nuclei at 81.03 and 162.00 MHz, respectively. Fine crystalline samples were packed into zirconium oxide rotors of 7 mm o.d. and 4 mm o.d. for low and high field experiments, respectively. The 2D ³¹P spin-echo spectrum of **5** was obtained on the Bruker MSL-200 NMR spectrometer with the conventional pulse sequence (*35*). The 2D data set was 128 by 512 and the 2D FT transformation was performed in the magnitude mode. All static ¹³C NMR spectra were obtained on Bruker MSL-200 and AMX-400 NMR spectrometers operating for ¹³C nuclei at 50.32 and 100.62 MHz, respectively. All static ¹⁵N NMR spectra were recorded on the Bruker MSL-200 NMR spectrometer operating for ¹⁵N nuclei at 20.32 MHz.

Cross polarization (CP) under the Hartmann-Hahn match and high-power proton decoupling were used in acquiring all aforementioned ¹³C, ¹⁵N and ³¹P NMR spectra. Typical 90° pulse widths were about 4.0 - 5.5 μ s and typical contact times were 2-5 ms. Recycle times ranged from 10 to 60 s.

Magic-angle-spinning (MAS) NMR experiments were also performed for all the compounds studied. Typical sample spinning frequencies ranged from 2 to 6 kHz for the low field experiments and 2 to 12 kHz for the high field ones. The magic angle was adjusted by examining the ⁷⁹Br NMR signal of a KBr sample (*101*).

All ³¹P NMR chemical shifts were referenced to 85% $H_3PO_4(aq)$ by using solid $NH_4H_2PO_4$, which has a resonance at +0.81 ppm relative to 85% $H_3PO_4(aq)$. All ¹³C NMR chemical shifts were referenced to TMS by using the secondary reference sample, adamantane. All ¹⁵N NMR chemical shifts were referenced to $NH_3(l)$ by setting the ¹⁵N NMR peak of solid ¹⁵NH₄NO₃ to 23.8 ppm.

Spinning sideband analysis was performed using a simplex program based upon

the method of Herzfeld and Berger (65). Typically, the relative intensities of six or seven spinning sidebands were used and three best-fit tensorial elements were obtained after a few iterations. The static powder lineshapes arising from homonuclear spin-pair systems were simulated with a FORTRAN program which incorporates the POWDER routine of Alderman *et al.* (102) for powder averaging. The simulations were based upon the exact analytical expression for a homonuclear spin pair, given by Eqs.(3.8)-(3.11). Both the direct dipolar and indirect spin-spin interactions were taken into account. Calculated lineshapes were usually convoluted with a Gaussian line-broadening function.

3.7 Conclusions

This chapter represents a detailed study of using dipolar-chemical shift NMR method to characterize chemical shift tensors in various types of homonuclear two-spin systems containing ${}^{31}P$, ${}^{13}C$ and ${}^{15}N$ nuclei in several classes of organic and organometallic compounds. Possible spectral features in NMR spectra arising from equivalent (A₂), first-order (AX) and second-order (AB) spin pairs have been investigated with experimental examples. For the first time, new spectral features associated with AB spin pairs have been clearly observed in NMR spectra of static solids.

Although the dipolar-chemical shift NMR technique was developed some time ago, its application has been very limited in the literature, especially for homonuclear spin systems. It has been demonstrated in this chapter that the information contents available in static NMR spectra of homonuclear spin systems, concerning chemical shift tensor and dipolar coupling constant, are useful to chemists in the study of local molecular structures and electronic environments in solid materials.

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Chapter 4

Magic-Angle-Spinning NMR Spectra of Homonuclear Two-Spin Systems

4.1 Introduction

Magic-angle-spinning (MAS) NMR spectroscopy has become a powerful technique for chemists to study solid materials. For magnetically dilute spin- $\frac{12}{2}$ nuclei such as 13 C, 15 N and 31 P, relatively sharp peaks are observed in NMR spectra acquired under conditions of high-power proton decoupling and MAS (*18,103*). These dilute spin systems are often treated as "isolated" spins. However, as has been shown in the previous chapter, it is common to have systems where a dilute spin is adjacent to another spin of the same magnetogyric ratio. If all of the abundant spins in the system are decoupled, the two dilute spins are said to constitute an "isolated" two-spin system or a spin pair.

Studies of MAS NMR spectra arising from isolated spin-pair systems were pioneered by Maricq and Waugh (104). In a seminal paper, they studied the ¹³C MAS NMR spectra of diammonium oxalate-¹³C₂, $(NH_4)_2(O_2^{13}C_2^{-13}CO_2)$. In this case, the two ¹³C nuclei in the oxalate anion can be treated as an isolated two-spin system, provided that high-power proton decoupling is used. They classified line broadening mechanisms in MAS NMR spectra into two categories: inhomogeneous and homogeneous. Broadening due to inhomogeneous interactions can easily be eliminated even with moderate sample spinning frequencies, whereas that due to homogeneous interactions cannot be removed completely unless the sample spinning frequency is greater than *all* anisotropic nuclear spin interactions present in the spin system under study. In particular, they showed the homonuclear ¹³C dipolar interaction in diammonium oxalate- $^{13}C_2$ is homogeneous, hence it causes broadening features in the ^{13}C MAS NMR spectra. The two ¹³C nuclei of solid diammonium oxalate- ${}^{13}C_2$ are crystallographically equivalent but magnetically non-equivalent. That is, although the two ¹³C nuclei have the same isotropic chemical shift, their chemical shift tensors have different orientations. Using average Hamiltonian theory (AHT) (26,104-106), Maricq and Waugh successfully reproduced the observed MAS NMR lineshapes. Furthermore, they predicted that MAS NMR spectra arising from such spin pairs are sensitive to the sample spinning frequency. This latter aspect of MAS NMR spectra has attracted considerable recent interest (60,61,107-111). For instance, Hayashi and Hayamizu (60), and Kubo and McDowell (61) independently reported that ³¹P MAS NMR spectra of $Na_4P_2O_7 \cdot 10 H_2O$ are sensitive to the sample spinning frequency. In particular, a single peak was observed at rapid and slow spinning frequencies while a doublet was observed at intermediate spinning frequencies. The splitting of the doublet was dependent on the sample spinning frequency in this intermediate regime. Kubo and McDowell (61) have presented theoretical expressions which can successfully account for the above observations in ³¹P MAS NMR spectra of $Na_4P_2O_7 \cdot 10 H_2O_1$.

In each of the aforementioned studies, the two crystallographically equivalent spins in the spin-pair systems are only coupled by the direct dipolar interaction. Another interesting phenomenon arises when two crystallographically equivalent but magnetically non-equivalent nuclei are also J coupled. As is well-known, the J coupling constant

between two spins with identical chemical shifts is not directly observable in isotropic fluids. In the solid state, however, the fact that chemical shift tensors of two crystallographically equivalent spins generally have different orientations makes it possible for the J interaction between the two spins with identical isotropic chemical shifts to be reintroduced into MAS NMR spectra. This phenomenon is known as Jrecoupling in MAS NMR spectra of solids. Although a J recoupling phenomenon between two crystallographically equivalent spins in MAS NMR spectra was predicted in the early paper of Maricq and Waugh (104), it was observed only recently by McDowell and co-workers (112-114). These latter authors noticed that ³¹P MAS spectra of 1,2-bis(2,4,6-tri-tert-butylphenyl)diphosphene (TBPDP) exhibit a general four-line pattern. They demonstrated that such J-recoupled MAS spectra can be understood by considering the average Hamiltonian and its first-order correction term. The J coupling constant can be measured directly from splittings in a J-recoupled spectrum. They concluded that the J recoupling effect between two crystallographically equivalent spins is promoted by the difference in their respective chemical shift tensor orientations and by the strength of the direct homonuclear dipolar coupling between the two spins. More recently, Eichele, Wu and Wasylishen (115) reported an unusual type of J-recoupled MAS spectra in ³¹P MAS NMR spectra of $Cd(PPh_3)_2(NO_3)_2$. The observed J-recoupled MAS spectra are unusual because ${}^{2}J({}^{31}P,{}^{31}P)$ is given by the separation between alternate lines in the four-line pattern, which is in contrast to the *J*-recoupled spectra of TBPDP. Also they noted that the observed unusual *J*-recoupled spectra cannot be predicted using the average Hamiltonian and its first-order correction term.

For homonuclear two-spin systems where the isotropic chemical shift difference between the two spins, ω_{Δ} , is large, interesting line-broadening effects and crossrelaxation behaviour are observed in MAS NMR spectra when ω_{Δ} matches a multiple of the sample spinning frequency, ω_R , *i.e.*, when $\omega_{\Delta} = n \omega_R$ where n is an integer. Such MAS NMR spectra are said to be obtained under rotational resonance (RR or R^2) conditions. More than 25 years ago, Andrew et al. (116,117) first recognized enhanced line broadening and cross relaxation in ³¹P MAS NMR spectra of solid PCl₅ [PCl₄ PC1₆] obtained under RR conditions. Recently, considerable attention has been devoted to investigations of MAS NMR spectra arising from homonuclear spin-1/2 pairs under RR conditions (118-129). Meier and Earl (108) observed frequency shifts and line broadening in ${}^{13}C$ MAS NMR spectra of zinc acetate- ${}^{13}C_2$ under conditions of RR. Colombo et al. (120) and Maas and Veeman (121) independently reported that ¹³C spindiffusion processes among natural abundant ¹³C nuclei can be dramatically enhanced between NMR resonances that satisfy the RR condition. A new method for internuclear distance determination has been developed by Griffin and co-workers (118,119). The method is mainly based on the fact that a significantly enhanced Zeeman magnetization exchange process occurs between two dipolar-coupled nuclei when NMR resonances of the coupled spins satisfy the RR condition. This method has been successfully applied to biologically important systems such as membrane proteins, peptides, enzyme-inhibitor complexes and reaction intermediates (130-134).

Although there have been many studies of homonuclear two-spin systems that can be treated using the AX approximation, only scattered experimental examples have appeared in the literature for systems where the two spins constitute a second-order (tightly *J*-coupled) spin pair, *i.e.*, the isotropic chemical shift difference of the two spins is smaller than or comparable to the *J* coupling constant between them. Analogous to solution state NMR studies, one may refer to such two-spin systems as AB spin systems. Harris *et al.* (*135,136*) noticed that peak intensities in ³¹P and ²⁰⁷Pb MAS NMR spectra of two different AB spin systems deviate from predictions based on formulae used in solution state NMR studies. Wu *et al.* (*137*) also observed unusual spinning sideband intensities in ³¹P MAS NMR spectra of RhH(CO)(PPh₃)₃ where the spin network is an ABMX system (A, B, M = ³¹P; X=¹⁰³Rh). In two-dimensional ³¹P *J*-resolved MAS NMR spectra of RhCl(PPh₃)₃, Wu and Wasylishen (*138*) noticed some anomalous features arising from AB spin systems. In a recent study, Challoner and McDowell (*139*) investigated MAS NMR spectra of the X spin in an ABX spin system.

The great success of the RR method in determining internuclear distances has inspired the development of several new techniques devoted to recovering weak homonuclear dipolar interactions from MAS NMR spectra. Tycko and Dabbagh (140) proposed a technique called DRAMA (dipolar recovery at the magic angle), which makes use of rotation-synchronized pulses. More recently, Tycko and Smith (141) developed general symmetry principles that can be used to design new DRAMA pulse sequences. Gullion and Vega (142) demonstrated the use of a technique called SEDRA (simple excitation for the dephasing of rotational-echo amplitudes) to extract dipolar couplings from MAS NMR spectra. Ok *et al.* (143) and Bennett *et al.* (144) obtained 2D correlation spectra under MAS conditions by using transverse and longitudinal mixing sequences, respectively.

Several theoretical treatments have been developed in order to describe MAS NMR spectra of a homonuclear spin- $\frac{1}{2}$ pair in the solid state. As already mentioned, for the first time Maricq and Waugh (*104*) demonstrated the power of average Hamiltonian theory in interpreting ¹³C MAS spectra arising from two dipolar-coupled spins. Meier and Earl (*108*) used an adiabatic approximation to treat observed line shifts and line broadening in ¹³C MAS spectra of zinc acetate-¹³C₂. Gan and Grant (*124*) proposed a pseudo-spin model to analyze the MAS spectra. In an extensive study, Levitt *et al.* (*125*) presented a numerical method for calculating MAS NMR spectra of homonuclear spin pairs. Recently, Schmidt and Vega (*128*), and Nakai and McDowell (*129*) have independently applied Floquet theory to provide a general description of MAS spectra.

In spite of a large number of studies associated with MAS NMR spectra of homonuclear two-spin systems, there has been no uniform treatment of the spinningfrequency dependence, a phenomenon recently observed in MAS NMR spectra. The objective of this chapter is to derive general theoretical expressions that can be used to interpret the spinning-frequency dependence observed in MAS NMR spectra.

The remainder of this chapter will be organized as follows. In §4.2 a uniform theoretical treatment based on the average Hamiltonian theory will be presented. Focus will be on the spinning-frequency dependence associated with MAS NMR spectra of homonuclear two-spin systems. In §4.3 novel spinning-frequency dependent MAS spectra will be reported for square-planar metal-phosphine complexes. In §4.4 *J*-

recoupling phenomenon under slow MAS conditions will be generalized. In §4.5 attention will be paid to detailed lineshapes in MAS spectra. §4.6 will be devoted to investigating MAS NMR spectra of general second-order spin systems. Experimental details will be given in §4.7 and a brief summary will appear in §4.8.

4.2 Theory

4.2.1 Effective Hamiltonian and MAS spectra

In the presence of a strong external magnetic field, the nuclear spin Hamiltonian for a pair of spin-¹/₂ nuclei can be written as:

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_{CS} + \mathcal{H}_D + \mathcal{H}_J \tag{4.1}$$

where \mathcal{H}_Z is the Zeeman interaction, \mathcal{H}_{CS} is the chemical shielding interaction, \mathcal{H}_D is the homonuclear dipole-dipole interaction and \mathcal{H}_J is the indirect spin-spin (*J*) interaction. In the absence of anisotropic *J* coupling, only \mathcal{H}_{CS} and \mathcal{H}_D depend on the orientation of a crystallite in the applied magnetic field. Under MAS conditions, the nuclear spin Hamiltonian becomes time-dependent (18):

$$\mathcal{H}(t) = -\omega_{1}(t)I_{1z} - \omega_{2}(t)I_{2z} + [2\omega_{d}(t) + \omega_{J}]I_{1z}I_{2z} + \frac{1}{2}[\omega_{J} - \omega_{d}(t)](I_{1+}I_{2-} + I_{1-}I_{2+})$$

$$(4.2)$$

where $\omega_i(t)$ (i = 1 and 2) and $\omega_d(t)$ are NMR frequencies arising from chemical shielding and the direct magnetic dipole-dipole interactions, respectively; ω_J is the isotropic J coupling constant in angular frequency units. The time-dependence of $\omega_i(t)$ (i = 1 and2) and $\omega_d(t)$ can be written as (18):

$$\omega_{i}(t) = C_{0}^{i} + C_{1}^{i} \cos(\gamma^{C} + \omega_{R}t) + S_{1}^{i} \sin(\gamma^{C} + \omega_{R}t) + C_{2}^{i} \cos 2(\gamma^{C} + \omega_{R}t) + S_{2}^{i} \sin 2(\gamma^{C} + \omega_{R}t) + C_{2}^{i} \cos 2(\gamma^{C} + \omega_{R}t) + S_{1}^{d} \sin(\gamma^{C} + \omega_{R}t) + C_{2}^{d} \cos 2(\gamma^{C} + \omega_{R}t) + S_{2}^{d} \sin 2(\gamma^{C} + \omega_{R}t)$$

$$(4.3)$$

$$+ C_{2}^{d} \cos 2(\gamma^{C} + \omega_{R}t) + S_{2}^{d} \sin 2(\gamma^{C} + \omega_{R}t)$$

$$(4.4)$$

where ω_R is the sample spinning frequency in angular frequency units. The coefficients C_0^i , C_1^i , C_2^i , S_1^i and S_2^i are functions of the orientation of the chemical shift tensors for spins i = 1 and i = 2, respectively; C_1^d , S_1^d , C_2^d and S_2^d are functions of the orientation of the dipolar interaction. Following Kubo and McDowell (61), the expressions for these coefficients are given below:

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$$C_0^i = \omega_0 \sigma_{iso}^i \tag{4.5}$$

$$C_{1}^{i} = \frac{\sqrt{2} \omega_{0}}{3} \left\{ -\frac{3}{2} (\sigma_{zz}^{i} - \sigma_{iso}^{i}) \sin 2\beta^{C} + 2(\sigma_{xz}^{i} \cos \alpha^{C} + \sigma_{yz}^{i} \sin \alpha^{C}) \cos 2\beta^{C} + \left[\frac{1}{2} (\sigma_{xx}^{i} - \sigma_{yy}^{i}) \cos 2\alpha^{C} + \sigma_{xy}^{i} \sin 2\alpha^{C} \right] \sin 2\beta^{C} \right\}$$
(4.6)

$$C_{2}^{i} = \frac{\omega_{0}}{3} \left\{ \frac{3}{2} (\sigma_{zz}^{i} - \sigma_{iso}^{i}) \sin^{2}\beta^{C} - (\sigma_{xz}^{i} \cos \alpha^{C} + \sigma_{yz}^{i} \sin \alpha^{C}) \sin 2\beta^{C} + \left[\frac{1}{2} (\sigma_{xx}^{i} - \sigma_{yy}^{i}) \cos 2\alpha^{C} + \sigma_{xy}^{i} \sin 2\alpha^{C} \right] (1 + \cos^{2}\beta^{C}) \right\}$$

$$(4.7)$$

$$S_{1}^{i} = \frac{\sqrt{2} \omega_{0}}{3} \left\{ 2(\sigma_{yz}^{i} \cos \alpha^{C} - \sigma_{xz}^{i} \sin \alpha^{C}) \cos \beta^{C} + 2 \left[\sigma_{xy}^{i} \cos 2\alpha^{C} - \frac{1}{2} (\sigma_{xx}^{i} - \sigma_{yy}^{i}) \sin 2\alpha^{C} \right] \sin \beta^{C} \right\}$$
(4.8)

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$$S_{2}^{i} = \frac{\omega_{0}}{3} \left\{ -2(\sigma_{yz}^{i} \cos \alpha^{c} - \sigma_{xz}^{i} \sin \alpha^{c}) \sin \beta^{c} + 2[\sigma_{xy}^{i} \cos 2\alpha^{c} - \frac{1}{2}(\sigma_{xx}^{i} - \sigma_{yy}^{i}) \sin 2\alpha^{c}] \cos \beta^{c} \right\}$$

$$(4.9)$$

$$C_{1}^{d} - \frac{\pi R_{DD}}{\sqrt{2}} [(1 - 3\cos^{2}\theta_{c})\sin 2\beta^{c} + 2\sin 2\theta_{c}\cos(\phi_{c} - \alpha^{c})\cos 2\beta^{c} + \sin^{2}\theta_{c}\cos 2(\phi_{c} - \alpha^{c})\sin 2\beta^{c}]$$
(4.10)

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$$C_2^{d} - \frac{\pi R_{DD}}{2} \left[\left(1 - 3\cos^2\theta_c \right) \sin^2\beta^c + \sin 2\theta_c \cos(\phi_c - \alpha^c) \sin 2\beta^c - \sin^2\theta_c \cos 2(\phi_c - \alpha^c) \left(1 + \cos^2\beta^c \right) \right]$$
(4.11)

$$S_1^d - \frac{2\pi R_{DD}}{\sqrt{2}} [\sin 2\theta_c \sin(\phi_c - \alpha^c) \cos \beta^c + \sin^2 \theta_c \sin 2(\phi_c - \alpha^c) \sin \beta^c] \quad (4.12)$$

$$S_2^d - \pi R_{DD} \left[\sin 2\theta_D \sin \left(\phi_c - \alpha^C \right) \sin \beta^C - \sin^2 \theta_C \sin 2 \left(\phi_c - \alpha^C \right) \cos \beta^C \right]$$
(4.13)

Usually, two transformations are defined to relate the crystal-axis-system (CAS), the rotor-axis-system (RAS) and the laboratory frame (LAB):

$$CAS \xrightarrow{\Re(\alpha^{c},\beta^{c},\gamma^{c})} RAS \xrightarrow{\Re(\omega_{R}t,54^{\circ}44^{\prime},0)} LAB$$

The orientation of the dipolar vector is defined in the CAS by (θ_c, ϕ_c) . The laboratory frame is defined by the applied magnetic field, **B**₀. The three referencing frames are shown in Fig.4.1.

From Eqs.(4.2)-(4.4), it is clear that the nuclear spin Hamiltonian in the MAS NMR experiment is periodic. To treat such a time-dependent periodic Hamiltonian, Waugh and co-workers have developed a successful method known as average

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Figure 4.1 The transformations relating the crystal-axis-system, the rotor-axis-system, and the laboratory frame.

Hamiltonian theory (AHT) (26,104-106). According to AHT, at $t = N T_R$ (T_R is the rotor period and N is an integer variable) the spin system can be described by an effective Hamiltonian, Eq.(4.14):

$$\mathcal{H}_{eff} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)} + \mathcal{H}^{(2)} + \cdots \qquad (4.14)$$

where

$$\mathcal{H}^{(0)} = \frac{1}{T_R} \int_0^{T_R} \mathcal{H}(t) dt$$
(4.15)

$$\mathfrak{H}^{(1)} = \frac{-i}{2T_R} \int_0^{T_R} dt_2 \int_0^{t_2} [\mathfrak{H}(t_2), \ \mathfrak{H}(t_1)] dt_1$$
(4.16)

$$\mathcal{H}^{(2)} = \frac{-1}{6T_R} \int_0^{T_R} dt_3 \int_0^{t_3} dt_2 \int_0^{t_2} \{ [\mathcal{H}(t_3), [\mathcal{H}(t_2), \mathcal{H}(t_1)] \} + [\mathcal{H}(t_1), [\mathcal{H}(t_2), \mathcal{H}(t_3)] \} dt_1$$
(4.17)

etc. The zeroth term, $\mathcal{H}^{(0)}$, is called the average Hamiltonian; $\mathcal{H}^{(1)}$ and $\mathcal{H}^{(2)}$ are the first and second-order correction terms, respectively. The expansion series of Eqs.(4.15)-(4.17) is called the Magnus expansion (145) and high-order terms can be derived. Substituting Eq.(4.2) into Eq.(4.15), one can obtain the average Hamiltonian:

$$\mathcal{H}^{(0)} = -\frac{\omega_{\Sigma}}{2} (I_{1z} + I_{2z}) - \frac{\omega_{\Delta}}{2} (I_{1z} - I_{2z}) + \omega_J I_1 \cdot I_2 \qquad (4.18)$$

where

$$\omega_{\Sigma} = \omega_{iso}^{1} + \omega_{iso}^{2} \quad and \quad \omega_{\Delta} = \omega_{iso}^{1} - \omega_{iso}^{2} \quad (4.19)$$

In this chapter, all the spin systems that will be treated satisfy the condition that the

isotropic chemical shift difference is much smaller than the sample spinning frequency, i.e., $\omega_{\Delta} \ll \omega_R$. This assures that no rotational resonance condition can be met for any practical sample spinning frequency, except for the special case of "n = 0 RR" (125). Under this condition, the first-order correction term is given by Eq.(4.20).

$$\mathfrak{H}^{(1)} = -iK_1 \frac{(I_{1+}I_{2-} - I_{1-}I_{2+})}{2}$$
(4.20)

where

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$$K_1 = \frac{1}{\omega_R} \left(-C_1^{\Delta} S_1^d + S_1^{\Delta} C_1^d - \frac{1}{2} C_2^{\Delta} S_2^d + \frac{1}{2} S_2^{\Delta} C_2^d \right) = \frac{k_1}{\omega_R}$$
(4.21)

The superscript Δ denotes the difference between corresponding coefficients, for example, $C_I^{\ \Delta} = C_I^{\ I} - C_I^{\ 2}$. After some lengthy but straightforward algebra, one can also obtain the second-order correction term as:

$$\mathfrak{H}^{(2)} = G_2 \frac{(I_{1z} - I_{2z})}{2} - F_2 \frac{(I_{1+}I_{2-} + I_{1-}I_{2+})}{2}$$
(4.22)

where

$$G_{2} = \frac{1}{96\omega_{R}^{2}} \left(7C_{1}^{\Delta}C_{1}^{d}C_{2}^{d} - 12C_{1}^{\Delta}S_{1}^{d}S_{1}^{d} + 12S_{1}^{\Delta}C_{1}^{d}S_{2}^{d} + 12S_{1}^{\Delta}S_{1}^{d}C_{1}^{d} - 4S_{1}^{\Delta}S_{1}^{d}C_{2}^{d} - 6C_{2}^{\Delta}C_{1}^{d}C_{2}^{d} + 4C_{2}^{\Delta}S_{1}^{d}S_{1}^{d} - 6C_{2}^{\Delta}S_{1}^{d}S_{2}^{d} - 3C_{2}^{\Delta}S_{2}^{d}S_{2}^{d} - 12S_{2}^{\Delta}C_{1}^{d}S_{1}^{d} + 6S_{2}^{\Delta}S_{1}^{d}C_{2}^{d} + 3S_{2}^{\Delta}C_{2}^{d}S_{2}^{d} \right)$$

$$= \frac{g_{2}}{\omega_{R}^{2}}$$

$$(4.23)$$

$$F_{2} = \frac{1}{48\omega_{R}^{2}} \left(7C_{1}^{d}C_{1}^{\Delta}C_{2}^{\Delta} - 12C_{1}^{d}S_{1}^{\Delta}S_{1}^{\Delta} + 12S_{1}^{d}C_{1}^{\Delta}S_{2}^{\Delta} + 12S_{1}^{d}S_{1}^{\Delta}C_{1}^{\Delta} - 4S_{1}^{d}S_{1}^{\Delta}C_{2}^{\Delta} - 6C_{2}^{d}C_{1}^{\Delta}C_{2}^{\Delta} + 4C_{2}^{d}S_{1}^{\Delta}S_{1}^{\Delta} - 6C_{2}^{d}S_{1}^{\Delta}S_{2}^{\Delta} - 3C_{2}^{d}S_{2}^{\Delta}S_{2}^{\Delta} - 12S_{2}^{d}C_{1}^{\Delta}S_{1}^{\Delta} + 6S_{2}^{d}S_{1}^{\Delta}C_{2}^{\Delta} + 3S_{2}^{d}C_{2}^{\Delta}S_{2}^{\Delta} \right)$$

$$= \frac{f_{2}}{\omega_{R}^{2}} \qquad (4.24)$$

Similarly, it can be shown that the 2n and (2n+1)th order correction terms to the average Hamiltonian have the following forms:

$$\Re^{(2n)} = G_{2n} \frac{(I_{1z} - I_{2z})}{2} + F_{2n} \frac{(I_{1+}I_{2-} + I_{1-}I_{2+})}{2}$$
(4.25)

$$\Re^{(2n+1)} = -iK_{2n+1} \frac{(I_{1+}I_{2-} - I_{1-}I_{2+})}{2}$$
(4.26)

where

$$G_{2n} = \frac{g_{2n}}{\omega_R^{2n}}, \quad F_{2n} = \frac{f_{2n}}{\omega_R^{2n}} \quad and \quad K_{2n+1} = \frac{k_{2n+1}}{\omega_R^{2n+1}}$$
 (4.27)

The coefficients g_{2n} , f_{2n} and k_{2n+1} are functions of the principle components of the two chemical shift tensors, the dipolar interaction and its orientation with respect to the chemical shift tensors. Although the explicit expressions for these coefficients may be complicated, it is useful to examine their magnitudes qualitatively. One can show that the following relationships hold in a qualitative sense.

$$g_{2n} \propto \Delta \cdot R_{DD}^{2n}$$
, $f_{2n} \propto \Delta^{2n} \cdot R_{DD}$, $n = 1, 2, 3, ...$ (4.28)

$$k_{2n+1} \propto \Delta^{2n+1} \cdot R_{DD}, \quad n = 0, 1, 2, 3, \dots$$
 (4.29)

where Δ is a quantity which depends on the difference between the two chemical shift tensors. These relationships will be useful in later discussions (§4.3.2).

Based on Eqs.(4.25) and (4.26), the effective Hamiltonian can be written as:

$$\begin{aligned} \mathcal{H}_{eff} &= \sum_{n=0}^{\infty} \mathcal{H}^{(n)} = \mathcal{H}^{(0)} + \sum_{n=1}^{\infty} \mathcal{H}^{(2n)} + \sum_{n=0}^{\infty} \mathcal{H}^{(2n+1)} \\ &= -\frac{\omega_{\Sigma}}{2} (I_{1z} + I_{2z}) - \frac{\omega_{\Delta}}{2} (I_{1z} - I_{2z}) + \omega_{J} I_{1} \cdot I_{2} \\ &+ G \frac{(I_{1z} - I_{2z})}{2} - F \frac{(I_{1+} I_{2-} + I_{1-} I_{2+})}{2} - iK \frac{(I_{1+} I_{2-} - I_{1-} I_{2+})}{2} \end{aligned}$$
(4.30)

where

$$G = \sum_{n=1}^{\infty} G_{2n} = \sum_{n=1}^{\infty} \frac{g_{2n}}{\omega_R^{2n}}$$
(4.31)

$$F = \sum_{n=1}^{\infty} F_{2n} = \sum_{n=1}^{\infty} \frac{f_{2n}}{\omega_R^{2n}}$$
(4.32)

$$K = \sum_{n=0}^{\infty} K_{2n+1} = \sum_{n=0}^{\infty} \frac{k_{2n+1}}{\omega_R^{2n+1}}$$
(4.33)

Using the product basis functions: $|1\rangle = |\alpha\alpha\rangle$, $|2\rangle = |\alpha\beta\rangle$, $|3\rangle = |\beta\alpha\rangle$ and $|4\rangle = |\beta\beta\rangle$, the effective Hamiltonian is usually expressed in a matrix form:

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$$\Theta_{eff} = \begin{pmatrix} -\frac{\omega_{\Sigma}}{4} + \frac{\omega_{J}}{4} & 0 & 0 & 0 \\ 0 & -\frac{\omega_{J}}{4} + \frac{G - \omega_{\Delta}}{2} & \frac{\omega_{J} - F}{2} - \frac{iK}{2} & 0 \\ 0 & \frac{\omega_{J} - F}{2} + \frac{iK}{2} & -\frac{\omega_{J}}{4} - \frac{G - \omega_{\Delta}}{2} & 0 \\ 0 & 0 & 0 & \frac{\omega_{\Sigma}}{4} + \frac{\omega_{J}}{4} \end{pmatrix}$$
(4.34)

Following steps analogous to those used in solving the "AB-spin problem" in solution NMR, the above matrix can be diagonalized, so that the four resonance frequencies and their relative intensities are obtained; Eqs.(4.35)-(4.38).

$$\omega_1 = \frac{1}{2} (\omega_{\Sigma} + D + \omega_J); \quad P_1 = 1 - \frac{\omega_J - F}{D}$$
 (4.35)

$$\omega_2 = \frac{1}{2} (\omega_{\Sigma} + D - \omega_J); \qquad P_2 = 1 + \frac{\omega_J - F}{D}$$
 (4.36)

$$\omega_3 = \frac{1}{2} (\omega_{\Sigma} - D + \omega_J); \qquad P_3 = 1 + \frac{\omega_J - F}{D}$$
 (4.37)

$$\omega_4 = \frac{1}{2} (\omega_{\Sigma} - D - \omega_J); \qquad P_4 = 1 - \frac{\omega_J - F}{D}$$
 (4.38)

where

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$$D = [(\omega_{\Delta} - G)^{2} + (\omega_{J} - F)^{2} + K^{2}]^{1/2}$$
(4.39)

Eqs.(4.35)-(4.39) are the key equations required to describe MAS NMR spectra of

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homonuclear two-spin systems.

It is important to emphasize that the effective Hamiltonian given by Eq.(4.14) can characterize the behaviour of spin systems only at $t = N T_R$, which corresponds to a spectrum obtained with data sampling synchronized with the rotor period. In ordinary MAS NMR experiments, however, the effective Hamiltonian can be used to describe the *total* MAS NMR line shape, which is a spectrum summed over all spinning sidebands.

4.2.2 Convergence of the Magnus expansion

In principle, the G, F and K terms in Eqs.(4.35)-(4.39) can contain high-order correction terms to any order. In practice, however, one is forced to take only the first few terms, *i.e.*, a truncated Magnus expansion series. Therefore, the convergence properties of the Magnus expansion play extremely important roles in determining the validity of the use of average Hamiltonian theory to describe MAS NMR spectra. The discussion which follows will be devoted to this subject.

Usually it is said that the Magnus expansion series should converge if the following equation holds (18):

$$h^{-1} \langle \mathcal{H}^2 \rangle^{1/2} T_R < 1$$
 (4.40)

However, as Maricq pointed out (146), this criterion ignores the structure of the spin Hamiltonian operator and can be misleading. For example, for a homonuclear two-spin system under the MAS condition, $\langle \mathcal{H}^2 \rangle^{1/2}$ is on the order of chemical shift anisotropy in frequency units, since chemical shift anisotropy is often much greater than the homonuclear dipolar interaction for dilute spins. Therefore, Eq.(4.40) indicates that the Magnus expansion series will not converge if the sample spinning frequency is smaller than the span of the chemical shift tensor (in frequency units). As will be shown in the subsequent sections, this criterion is far too restrictive.

It is known that choosing a correct interaction representation can improve the convergence condition of the Magnus expansion. Levitt *et al.* (125) recently suggested the separation of the total spin Hamiltonian into two parts:

$$\mathcal{H}(t) = \mathcal{H}_{0}(t) + \mathcal{H}_{1}(t) \tag{4.41}$$

where $\mathcal{H}_0(t)$ is inhomogeneous and always commutes with $\mathcal{H}_1(t)$. The term $\mathcal{H}_1(t)$ is however homogeneous. In fact, a similar separation occurs naturally in the Magnus expansion even when the total spin Hamiltonian is used. For example, consider the commutator for the first-order correction term.

$$[\mathcal{H}(t_1), \mathcal{H}(t_2)] = [\mathcal{H}_0(t_1) + \mathcal{H}_1(t_1), \mathcal{H}_0(t_2) + \mathcal{H}_1(t_2)]$$

=
$$[\mathcal{H}_1(t_1), \mathcal{H}_1(t_2)]$$
(4.42)

Similarly, all high-order correction terms will have commutators that contain only \mathcal{H}_1 . Therefore, for a two-spin system in MAS experiments, the convergence properties of the Magnus expansion will be determined only by \mathcal{H}_1 rather than by the total spin Hamiltonian, $\mathcal{H}_0 + \mathcal{H}_1$.

It can be shown that the homogeneous part of the effective Hamiltonian given in Eq.(4.2), \mathcal{H}_1 , has the following form (125):

$$\mathcal{H}_{1}(t) = \left[\omega^{1}(t) - \omega^{2}(t) \right] I_{z}^{(23)} + \left[\omega_{J} - \omega_{d}(t) \right] I_{x}^{(23)}$$
(4.43)

where $I_z^{(23)}$ and $I_x^{(23)}$ are single-transition operators. Therefore, the original convergence

problem associated with the total spin Hamiltonian is now reduced to a two-level system in the $\{|2\rangle, |3\rangle\}$ subspace. To treat such a two-level system, Maricq (146) recently proposed a general criterion for the convergence of the Magnus expansion. By applying Maricq's theory, the criterion is given by:

$$\frac{1}{2\pi} \int_{0}^{T_{R}} |\omega^{1}(t) - \omega^{2}(t)| dt < 1$$
(4.44)

The physical insight of this equation is very clear. The convergence condition of the Magnus expansion series depends only on the difference between the two chemical shift tensors rather than the spans of the chemical shift tensors. This criterion is much more relaxed than that given by Eq.(4.40).

For a powder sample, Eq.(4.44) can be evaluated numerically if one knows the orientation of the chemical shift tensors. However, to provide direct physical pictures, the following two simpler criteria are useful: (1) the largest instantaneous chemical shift difference for a static powder sample, Δ_{max} , or (2) the time-averaged value of Δ_{max} , $<\Delta_{max}(t)>$, for a particular crystallite undergoing MAS. To gain some insight about these two convergence conditions, consider the case of *cis*-azobenzene-¹⁵N₂ dioxide. Based on the nitrogen chemical shift tensors determined in §3.5.1, the span of the chemical shift tensor in frequency units is about 5.4 kHz at 4.70 T, *i.e.*, $h^{-1} < \mathcal{H}^2 > ^{1/2} \sim 5.4$ kHz. The two ¹⁵N nuclei have the largest chemical shift difference when the external magnetic field lies in the molecular plane making an angle of 45° with respect to the N-N bond, $\Delta_{max} = 2.6$ kHz. Consider that this particular crystallite is spun about an axis that also lies in the molecular plane and makes the magic angle with respect to

the external field. Now the chemical shift difference becomes time-dependent. It is straightforward to show that $\Delta_{max}(t)$ has the following form:

$$\Delta_{\max}(t) = \frac{1}{2\pi} [\omega_1(t) - \omega_2(t)]$$

$$= \Delta_{\max} (0.89 \cos \omega_R t - 0.11 \cos 2\omega_R t)$$
(4.45)

Using the criterion of Eq.(4.44), $<\Delta_{max}(t)>$ can be evaluated:

$$\left\langle \Delta_{\max}(t) \right\rangle = \frac{1}{2\pi} \int_{0}^{T_{R}} |\omega^{1}(t) - \omega^{2}(t)| dt$$

$$= \Delta_{\max} \int_{0}^{T_{R}} |0.89 \cos \omega_{R} t - 0.11 \cos 2\omega_{R} t | dt$$

$$(4.46)$$

The criteria of Δ_{max} and $\langle \Delta_{max}(t) \rangle$ indicate that the convergence conditions of the Magnus expansion series are much more relaxed than Eq.(4.40). In Fig.4.2, $\Delta_{max}(t)$ is plotted and it is straightforward to obtain the result: $\langle \Delta_{max}(t) \rangle = 0.57 \Delta_{max}$. All three criteria are compared in Fig.4.3. As will be shown in §4.5, the spinning frequency limits derived from Δ_{max} and $\langle \Delta_{max}(t) \rangle$ are reasonable convergence conditions for the Magnus expansion series.







Figure 4.3 Three convergence conditions for the Magnus expansion series.

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4.3 Spinning-frequency dependent ³¹P MAS spectra of square-planar metalphosphine complexes

In this section, the spin systems to be treated will be homonuclear two-spin systems where the two spins are only coupled by the dipolar interaction. More specifically, two ³¹P nuclei that are cis to one another in typical square-planar metal-phosphine complexes will be examined.

4.3.1 Spinning-frequency dependent MAS spectra

Phosphorus-31 MAS NMR spectra of bis(methyldiphenylphosphine)(1,5cyclooctadiene)iridium(I) hexafluorophosphate, $[Ir(PPh_2Me)_2(COD)][PF_6]$ (13), obtained at three different sample spinning frequencies are shown in Fig.4.4. With a sample spinning frequency of 6.5 kHz, the ³¹P MAS NMR spectrum of 13 obtained at 4.70 T consists of a single strong peak flanked by weak spinning sidebands. This indicates that the sample spinning frequency is comparable to the anisotropic nuclear spin interactions, which in the case of 13 is dominated by the anisotropic ³¹P chemical shift. Compound 13 is expected to be square-planar with the two phosphine ligands cis to one another; observation of a single peak in the ³¹P MAS NMR spectra obtained at the rapid spinning limit implies that the two mutually cis ³¹P nuclei are crystallographically equivalent with an isotropic chemical shift of 1.03 ppm. Carbon-13 CP/MAS and dipolar-dephased experiments were also carried out for 13. The two methyl groups in 13 give rise to a single ¹³C peak with an isotropic carbon chemical shift of 15.5 ppm, providing further evidence for the crystallographic equivalence of the two phosphine ligands. Apparently,



Figure 4.4 Phosphorus-31 MAS NMR spectra of $[Ir(PPh_2Me)_2(COD)][PF_6]$ (13) obtained at 4.70 T with different sample spinning frequencies. The low-frequency septet centred at -143 ppm due to PF_6^- with ${}^1J({}^{31}P, {}^{19}F) = 712$ Hz is not shown.

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the crystal structure of 13 has not been determined by X-ray crystallography.

Interestingly, the ³¹P MAS NMR spectrum of 13 obtained with a spinning frequency of 3.5 kHz exhibits a doublet with the peak-to-peak splitting being equal to 103 + 6 Hz (Fig.4.4). In fact, doublets are observed in the ³¹P MAS NMR spectra in the spinning frequency range of 2.0-5.5 kHz with the splitting of the doublet being sensitive to the spinning frequency. The peak-to-peak splittings range from 60 to 107 Hz. At very slow spinning frequencies ($\omega_R/2\pi < 1.5$ kHz), the doublet collapses to a single peak. In Fig.4.5, the isotropic portions of the ³¹P MAS NMR spectra of 13 obtained at two different applied magnetic fields, 4.70 and 9.40 T, are displayed for The ³¹P MAS NMR spectra of 13 at 9.40 T show similar spinningcomparison. frequency dependent behaviour to that observed at 4.70 T. At spinning frequencies higher than 9.0 kHz, a single peak is observed. At intermediate spinning frequencies, from 4 to 9 kHz, doublets are observed in the ³¹P MAS NMR spectra. For example, at a sample spinning frequency of 7.5 kHz, the peak-to-peak splitting of the doublet is 96 \pm 6 Hz (see Fig.4.5). When the sample spinning frequency is decreased below 4 kHz, the doublet collapses to a single peak.

It is convenient to compare MAS NMR spectra obtained at 4.70 and 9.40 T by introducing a scaled sample spinning frequency, ω_R^{scaled} , defined as:

$$\omega_R^{scaled} = \omega_R \left[\frac{4.70}{B_0} \right] \tag{4.47}$$

In Fig.4.6 the peak-to-peak splittings in the ³¹P MAS NMR spectra are plotted as a function of the scaled sample spinning frequencies. It is interesting to note that the two



Figure 4.5 Expansions of the isotropic region of the ${}^{31}P$ MAS NMR spectra of $[Ir(PPh_2Me)_2(COD)][PF_6]$ (13) obtained at 4.70 T and 9.40 T.

curves shown in Fig.4.6 are approximately coincident. That is, the spinning-frequency dependence of the ³¹P MAS NMR spectra of **13** is *independent* of the applied magnetic field, provided that scaled spinning frequencies are used.



Figure 4.6 Plot of the peak-to-peak splitting against the scaled sample spinning frequency in the ³¹P MAS NMR spectra of [Ir(PPh₂Me)(COD)][PF₆] (13) at 4.70 and 9.40 T.

It is also worth mentioning that multiplets due to ${}^{1}J({}^{31}P, {}^{191/193}Ir)$ have not been observed in the ${}^{31}P$ MAS NMR spectra of iridium(I)-phosphine complexes (147,148), even though both naturally occurring isotopes of iridium are magnetically active, ${}^{191}Ir$ (I = 3/2, NA = 37.3%) and ${}^{193}Ir$ (I = 3/2, NA = 62.7%). Both of these isotopes have

very large quadrupole moments hence quadrupolar relaxation is expected to be extremely efficient, particularly at ambient temperature. Rapid quadrupolar relaxation of the iridium nuclei will lead to "self-decoupling". For the same reason, ${}^{31}P$, ${}^{201}Hg$ spin-spin splittings are rarely observed in ${}^{31}P$ CP/MAS spectra of mercury phosphine complexes even though the values of ${}^{1}J({}^{31}P, {}^{201}Hg)$ are known to be large (149).

The isotropic part of a typical ³¹P MAS NMR spectrum of cis-Pt(PEt₃)₂Cl₂ (14) is shown in Fig.4.7. The spectrum consists of two intense central peaks flanked by satellite peaks which arise from indirect spin-spin coupling with ¹⁹⁵Pt (I = ¹/₂, NA = 33.8 %); ¹J(¹⁹⁵Pt, ³¹P) = 3.4 kHz. The observation of two intense central peaks in the ³¹P MAS NMR spectrum of 14 appears to be consistent with the structure derived from



Figure 4.7 Isotropic region of the ³¹P MAS NMR spectrum of *cis*-Pt(PEt₃)₂Cl (14) at 9.40 T. The sample spinning frequency was 9000 Hz.

X-ray diffraction studies, which indicate that the two phosphorus nuclei are crystallographically non-equivalent (150). However, it is interesting to note that the peak-to-peak splitting of the doublet is sensitive to the sample spinning frequency (111).

The spinning-frequency dependence of the splitting observed at 4.70 T (see Fig.4.8) is quite similar to that observed for **13** where the two ³¹P nuclei are crystallographically equivalent. Therefore, it is dangerous to conclude that the two ³¹P nuclei of **14** are crystallographically non-equivalent simply because a doublet is observed. To further study the spinning-frequency dependence of the ³¹P MAS NMR spectra of **14**, variable spinning frequency ³¹P MAS experiments were performed at a higher magnetic field, 9.40 T. At 9.40 T the ³¹P MAS NMR spectra of **14** also exhibit spinning-frequency dependence of **13**, the peak-to-peak splitting of the doublet increases by a factor of approximately 1.5 at the higher field (see Fig.4.8). In addition,



Figure 4.8 Plots of the peak-to-peak splitting vs. the scaled sample spinning frequency in ³¹P MAS NMR spectra of *cis*-Pt(PEt₃)₂Cl₂ (14) at 4.70 and 9.40 T.

the sensitivity of the peak-to-peak splitting to the sample spinning frequency is considerably reduced for ${}^{31}P$ MAS NMR spectra at the higher field (*vide infra*).

4.3.2 Crystallographic equivalence and MAS spectra

In this section, qualitative rationalizations for the observations in the ³¹P MAS NMR spectra of the above two complexes will be provided on the basis of the general expressions for peak positions and relative intensities of MAS NMR spectra derived in §4.2. It is well-known that for square-planar bisphosphine complexes of iridium(I) and platinum(II) metals, ${}^{2}J({}^{31}P,{}^{31}P)_{cis}$ is usually too small to be observed in one-dimensional ${}^{31}P$ CP/MAS spectra (138,151-155). Assuming ${}^{2}J({}^{31}P,{}^{31}P)_{cis} = 0$, the four allowed transitions derived for a general "AB" spin pair (Eqs.(4.35)-(4.38)) reduce to two transitions with equal intensity. The separation of the two peaks, *D*, can be written in angular frequency units as:

$$D = [(\omega_{\Delta} - G)^{2} + F^{2} + K^{2}]^{1/2}$$
(4.48)

In the fast spinning limit, $\omega_R \rightarrow +\infty$, the high-order terms K, F and G approach zero and the separation between the two peaks equals the isotropic chemical shift difference, *i.e.*, $D = \omega_{\Delta}$; see Eq.(4.48). At slower spinning frequencies, *i.e.*, when the sample spinning frequency is smaller than the chemical shift anisotropies, the high-order terms K, F and G become important and they introduce additional shifts for the two peaks in MAS spectra. Since the high-order terms are cross terms between the homonuclear dipolar interaction and the anisotropic chemical shift interaction, they are proportional to

products of both interactions (see Eqs.(4.28) and (4.29)). Therefore, the additional shifts due to small dipolar couplings can be amplified by coupling to relatively large chemical shift anisotropies. For example, while ³¹P-³¹P homonuclear dipolar coupling constants are on the order of 300-500 Hz for two mutually cis phosphorus nuclei in square-planar metal-phosphine complexes, ³¹P chemical shift anisotropies are usually on the order of 50-100 ppm corresponding to 4-8 kHz at 4.70 T. Under such circumstances, the separation between the two peaks in MAS spectra differ from the actual isotropic chemical shift difference between the two nuclei. Clearly, since the high-order terms K, F and G are sensitive to the sample spinning frequency, the resultant additional shifts for the two peaks are also dependent upon the sample spinning frequency leading to a spinning-frequency dependent splitting. Only at the rapid spinning limit, *i.e.*, when the spinning frequency is much greater than all anisotropic nuclear spin interactions, do MAS NMR spectra correspond to solution NMR spectra. The relative intensities of the spinning sidebands to the isotropic peaks provide an indication of whether or not the rapid spinning limit has been achieved.

For a spin pair containing two crystallographically equivalent ³¹P nuclei, the implication of Eq.(4.48) is more interesting. In this case, even though the isotropic chemical shift difference between the two ³¹P nuclei vanishes, *i.e.*, $\omega_{\Delta} = 0$, it is still possible to observe two peaks in ³¹P MAS spectra (60,61). The peak-to-peak splitting in ³¹P MAS NMR spectra can be written as:

$$D = \left[G^2 + F^2 + K^2 \right]^{1/2} \tag{4.49}$$

This splitting results from high-order terms and is sensitive to the sample spinning

frequency. When the rapid spinning condition is satisfied, K, F and G approach zero and a single peak results. Under slow spinning conditions, however, two peaks will be observed in MAS spectra.

As has been noticed in Fig.4.6 and Fig.4.7, the reas to-peak splittings for compounds 13 and 14 behave differently as the strength of the applied magnetic field is changed. Since this different field dependence yields valuable information concerning the crystallographic equivalence between the two coupled nuclei, a more detailed discussion is necessary.

From Eqs.(4.28) and (4.29) it is clear that if Δ is much greater than R_{DD} , the g_{2n} terms are less important than the terms k_{2n+1} and f_{2n} . On the other hand, the term g_{2n} will contribute significantly to D if $\Delta \ll R_{DD}$. It is important to note that when the scaled spinning frequency is used, k_{2n+1} and f_{2n} are *independent* of the applied magnetic field, whereas g_{2n} is proportional to $(1/\omega_o)^{2n-1}$. For two ³¹P nuclei that are cis to one another in typical square-planar complexes, the g_{2n} terms are usually negligible. In Fig.4.6 the observation of two approximately coincident curves implies that the g_{2n} correction terms are indeed negligible for 13; therefore in this case, D is independent of the applied magnetic field. It is a general observation that the MAS line-widths increase in frequency units (Hz) with the applied magnetic field. This may obscure splittings at high magnetic fields. As expected, for the ³¹P MAS NMR spectra of 13 at the high field, 9.40 T, the line-widths are slightly greater than those at 4.70 T and the two peaks are less resolved, although the corresponding peak-to-peak splittings are essentially the same for the spectra at both fields.

When two ³¹P nuclei are crystallographically non-equivalent, as is the case for compound 14, the presence of the isotropic chemical shift difference term, ω_{Δ} , in Eq. (4.48) will introduce a different field dependence for the peak-to-peak splitting in ³¹P MAS NMR spectra. Since ω_A is doubled in frequency units by increasing the magnetic field strength from 4.70 to 9.40 T, the splitting of the doublet, D, is also increased (see Fig.4.8). However, since D also contains high-order terms K and F, which are independent of the applied magnetic field, the overall increase in D is attenuated compared with the actual field increase. For the case of compound 14, where the two coupled ³¹P nuclei are crystallographically non-equivalent, D increases approximately by a factor of 1.5 as the applied field strength is doubled. Only at the rapid spinning limit when the splitting approaches the actual isotropic chemical shift difference does the ratio between splittings obtained at different fields correspond to the ratio of the applied fields. It is readily seen in Fig.4.8 that, at the rapid spinning limit, the peak-to-peak splitting approaches 100 and 200 Hz for the data obtained at 4.70 and 9.40 T, respectively. These values yield the actual isotropic chemical shift difference, 1.23 ppm. Having established that the two phosphine ligands in 14 are crystallographically non-equivalent, it is clear that the values of ${}^{1}J({}^{31}P, {}^{195}Pt)$ are 3423 and 3469 Hz for the high and low frequency peaks, respectively.

Another interesting feature associated with the field dependence of the peak-topeak splitting in MAS spectra of compound 14 is the sensitivity of the splitting to the sample spinning frequency. As the spinning-frequency dependence of MAS NMR spectra results only from high-order correction terms, a large ω_{Δ} will reduce the relative contributions from high-order correction terms and therefore will quench the spinningfrequency dependence of D (see Eqs.(4.48) and (4.49)). Therefore, the sensitivity of the peak-to-peak splitting to the spinning frequency for ³¹P MAS NMR spectra of 14 is considerably reduced by carrying out the MAS experiment at a higher field. If even higher fields are used, ω_{Δ} may become large enough to completely quench the spinningfrequency dependence of the MAS NMR spectra.

In summary, one has seen that doublets may be observed in ³¹P MAS NMR spectra of typical square-planar metal-phosphine complexes *regardless* of the crystallographic equivalence of the two cis phosphine ligands. In either case the peak-to-peak splitting of the doublet may be sensitive to the sample spinning frequency hence care must be exercised in deducing whether or not two ³¹P nuclei are crystallographically equivalent. The first example of this kind was reported by Hayashi and Hayamizu (*60*) and by Kubo and McDowell (*61*) in ³¹P MAS spectra of Na₄P₂O₇ · 10 H₂O where the two ³¹P nuclei are crystallographically equivalent. However, it appears that previous researchers did not realize that MAS spectra arising from two non-equivalent spins can also exhibit a similar spinning-frequency dependence. Here a uniform treatment is presented.

The phenomena reported here are expected to occur frequently in ³¹P MAS NMR spectra of other metal-phosphine complexes whenever two ³¹P nuclei are adjacent to one another. In fact, ³¹P MAS NMR spectra of several metal-phosphine complexes exhibit two closely separated peaks (*153*); it is also a common practice to correlate the number of peaks observed in ³¹P MAS NMR spectra with the number of phosphorus atoms in the

asymmetric unit determined from X-ray crystallography studies. However, in light of the present study, many of the previous ³¹P MAS NMR spectra may need to be reexamined. If the rapid spinning limit cannot be reached in practice, it is important to study ³¹P MAS NMR spectra by varying the sample spinning frequency over a large range. In addition, carrying out MAS NMR experiments at different fields proves to be an effective way to eliminate the ambiguity concerning the crystallographic equivalence of the ³¹P nuclei.

4.4 *J*-recoupling patterns arising from two crystallographically equivalent spins

In §4.3, MAS NMR spectra of homonuclear two-spin systems where the two spins are only dipolar coupled to one another have been investigated. In this section, cases where both dipolar and J interactions between two crystallographically equivalent spins are present in the spin pair will be investigated.

4.4.1 The three types of *J*-recoupling patterns

One of the important implications of Eqs.(4.35)-(4.39) is that, under *slow* MAS conditions, the NMR spectrum of two crystallographically equivalent spins ($\omega_{\Delta} = 0$) can give rise to a general four-line spectrum for a powder sample. In contrast, only a single peak would be observed for an isotropic liquid sample or for a powder sample spinning rapidly at the magic angle. Since an analysis of such four-line spectra is capable of yielding the *J* coupling between two crystallographically equivalent spins, the slow MAS spectra are referred to as *J*-recoupled spectra (*112-114*). Equally important is the fact

that the appearance of the four-line pattern is dependent on the sample spinning frequency, ω_R . A plot of the peak positions in the four-line pattern as a function of sample spinning frequency is referred to as a *J*-recoupling pattern in this thesis.

Before proceeding to investigations on J-recoupling patterns, several common features of J-recoupled spectra described by Eqs. (4.35)-(4.39) are worth mentioning at this stage. First, the chemical shift tensors of the two crystallographically equivalent spins must be non-coincident in order to observe J-recoupled spectra. Second, dipolar coupling between the two homonuclear spins is essential to recouple the J interaction. Of course, if the anisotropy in the J tensor is large, it is also possible to observe Jrecoupling even in the absence of the dipolar interaction. However, it is assumed in this chapter that the anisotropy in the J tensor is negligible. Third, at the high spinning frequency limit, the two central lines in the *J*-recoupled spectra collapse to the isotropic chemical shift, ω_{iso} , while the two outer lines vanish at $\omega_{iso} \pm \omega_J$. It is also worth noting that, since the MAS experiments for a pair of crystallographically equivalent spins satisfy the condition for a "n = 0 RR" at any spinning frequency, the four transitions derived in §4.2 (Eqs. (4.35)-(4.38)) are similar to the general eight-line patterns derived by Levitt et al. (125) under RR conditions using Floquet theory. Since the isotropic chemical shift difference vanishes for a pair of crystallographically equivalent spins, the two central levels in the general four-level system become degenerate. A resonant splitting of them leads to only four observable single-quantum transitions between the virtual states and the two outer levels. Interestingly, the even-order correction terms introduce a shift for the state |2> and |3>, *i.e.*, $G(I_{1z} - I_{2z})/2 = G I_z^{(23)}$. This shift is directly analogous to the Bloch-Siegert shift (156) as noted by Levitt *et al.* (125). Also, the even-order correction terms introduce an additional component, F, which could reduce the apparent J coupling constant. It will be shown in the following that this additional term is responsible for the variations in different types of J-recoupling patterns.

It is interesting to note that Eqs.(4.35)-(4.39) are similar to those which result from solving the AB problem in solution NMR studies, except that the isotropic chemical shift difference vanishes in the solid state systems considered here, and the mixing term, D, has a different form. As is well-known in solution NMR, the ratio of the mixing term, D, to the J coupling constant, ω_J , determines the general appearance of the AB spectrum. Different magnitudes of the mixing term, D, compared to ω_J will result in three basic types of J-recoupling patterns. However, before we discuss these, it is useful to first examine the magnitude of D as a function of sample spinning frequency.

It is readily seen in Eq.(4.39) that if only the average Hamiltonian, $\mathcal{H}^{(0)}$, is considered, *i.e.*, K = G = F = 0, the *D* term is independent of sample spinning frequency and always equals ω_J . When the first-order correction term, $\mathcal{H}^{(1)}$, is added, *D* becomes greater than ω_J , *i.e.*, $(\omega_J^2 + K_I^2)^{1/2} \ge \omega_J$. As the spinning frequency increases, *D* decreases monotonically until it reaches ω_J at the high spinning limit. When the second-order correction term, $\mathcal{H}^{(2)}$, is further included, the *D* term is given by:

$$D = \left[G_2^2 + \left(\omega_J - F_2 \right)^2 + K_1^2 \right]^{1/2}$$

$$= \left[\frac{g_2^2}{\omega_R^4} + \left(\omega_J - \frac{f_2}{\omega_R^2} \right)^2 + \frac{k_1^2}{\omega_R^2} \right]^{1/2}$$
(4.50)

Based on the above equation, it becomes possible for the *D* term to be smaller than ω_j in a range of spinning frequencies because of the introduction of the F_2 term. Figure 4.9 shows schematically the magnitude of *D* as a function of sample spinning frequency when different correction terms in the effective Hamiltonian are considered. Note that the bottom curve in Fig.4.9 illustrates the effect of including the second-order correction term in just one possible case, *i.e.*, for a particular set of k_1 , g_2 , f_2 and ω_j values. The bottom curve containing the second-order correction can also be similar to that obtained by considering only the first-order correction term, provided the second-order correction term is not large enough to make the *D* term smaller than ω_j . However, it is the curve shown that causes the *unusual* appearance of the *J*-recoupled spectra, which will be discussed below.

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Figure 4.9 A schematic diagram illustrating the MAS frequency dependence of the mixing term D when different order correction terms are considered.

In general, there are three possible types of *J*-recoupling patterns depending on the magnitude of the mixing term, *D*, compared with ω_J :

- (I) $D > \omega_J$,
- (II) $D < \omega_J$ and

(III) $D > \omega_J$ at slow spinning frequencies while $D < \omega_J$ at high spinning frequencies.

The spinning-frequency dependence of these three distinctive types of J-recoupling patterns are sketched in Fig.4.10. In the discussion which follows, a detailed description of these three types of J-recoupling patterns will be presented.

In the type I J-recoupling pattern, where $D > \omega_J$, the four-line spectrum is analogous to the AB spectrum predicted in solution NMR. This type of pattern is referred to as a usual J-recoupled spectrum. In usual J-recoupled spectra, the J coupling constant is always given by the separation of the outer two peaks in the four-line pattern independent of ω_R . As shown in Fig.4.10(a), the separation between ω_I and ω_2 (as well as that between ω_3 and ω_4) equals ω_J , so that these frequency differences are independent of ω_R . At the high spinning limit, the two central peaks collapse and the intensities of the outer peaks vanish, leading to a single peak at the position of the isotropic chemical shift. At slower spinning frequencies, the central peak splits with two non-vanishing outer peaks, leading to a four-line spectrum. As the sample spinning frequency decreases, the low and high frequency parts of the four-line spectrum move apart from each other with the two outer lines becoming more intense. Note that as the sample spinning frequency decreases, the separation between the two outer peaks



Figure 4.10 A schematic diagram illustrating each of the three types of *J*-recoupling patterns. (a) Type I, (b) Type II, and (c) Type III.

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increases. The type I J-recoupling pattern was first observed in the ³¹P CP/MAS spectra of TBPDP by McDowell and co-workers (112-114).

In the type II J-recoupling pattern, where $D < \omega_J$, the two central lines in the four-line spectrum interchange their relative positions. Consequently, the J coupling constant is given by the separation between alternate peaks, *i.e.*, between ω_I and ω_2 or ω_3 and ω_4 , rather than by the two outer splittings in the usual J-recoupled spectra (type I). Since this situation can never be observed in solution NMR studies, we denote this type of J-recoupling pattern as *unusual*. At the high spinning limit, a single peak is also observed at the position of the isotropic chemical shift. At slower spinning frequencies, a general four-line pattern appears. In contrast to the situation in the usual J-recoupling pattern (type I), however, the separation between the two outer peaks in the unusual J-recoupling pattern *decreases* as the sample spinning frequency decreases. The first observation of such an unusual J-recoupling pattern has recently been reported by Eichele, Wu and Wasylishen (115). They observed spinning-frequency dependent splittings in the ³¹P CP/MAS spectra of Cd(PPh_3)₂(NO₃)₂.

In the type III J-recoupling pattern, $D - \omega_J$ changes sign at a specific spinning frequency, and the resultant pattern can be thought of as a combination of the type I and II patterns. At the rapid spinning extreme, similar to the cases in type I and II patterns, the MAS spectrum consists of a single isotropic peak centred at the isotropic chemical shift position. As the spinning frequency decreases, but still lies in the high frequency regime, the four-line spectrum exhibits the same behaviour as that in the unusual *J*recoupling pattern, *i.e.*, the *J* coupling constant is given by the separation between

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alternate peaks and the separation between the two outer peaks decreases as the spinning frequency decreases. However, after the spinning frequency reaches a certain value, at which the D term reaches its minimum, the separation between the two outer peaks starts to increase as the spinning frequency decreases. As the sample spinning frequency is further reduced, the two central peaks merge, giving rise to a three-line pattern and then cross as the MAS frequency enters the slow spinning regime. In this regime the J coupling constant is given by the separation between the two adjacent outer peaks in the four-line spectrum, *i.e.*, a usual J-recoupled spectrum. The spinning frequency dependence of the complete pattern looks rather complicated. To date this type of J-recoupling pattern has not been observed. Based on Eqs.(4.28), (4.29) and (4.35)-(4.39), it is apparent that this type of recoupling pattern will only be observed in extreme situations (*vide infra*).

From Eqs.(4.35)-(4.39) it is clear that not only do the peak positions in a *J*-recoupled spectrum change as a function of sample spinning frequency, but also the relative intensities of the four lines. Since the *J*-recoupled spectrum is always symmetric, as indicated by Eqs.(4.35)-(4.39), it is only necessary to discuss the relative intensities of the peaks within the four-line patterns. Here we define the intensity ratio of the outer peaks to the inner peaks by the parameter *S*. Since the two central peaks always have equal intensity, a switch in their relative positions in the different types of *J*-recoupled spectra does not change *S*. Hence, it is unnecessary to make a distinction between the different types of *J*-recoupling patterns when discussing the relative intensities of the peaks. Because *D* approaches ω_J at the high spinning frequency limit,

it leads to a vanishing S. Under such conditions, the J coupling constant will not be observable. As the sample spinning frequency decreases, S increases, *i.e.*, the outer lines become more intense at slower spinning frequencies. Thus a four-line pattern results and the J coupling constant is reintroduced. A schematic plot of S against the sample spinning frequency is shown in Fig.4.11.



Figure 4.11 A schematic diagram illustrating the MAS frequency dependence of the relative intensity within *J*-recoupled spectra.

4.4.2 Results and discussion

Unusual J-recoupled spectra. The ³¹P CP/MAS spectra of Hg(PPh₃)₂(NO₃)₂ (15) as a function of the sample spinning frequency at 4.70 T are shown in Fig.4.12. Note that each spectrum is the *total* MAS NMR spectrum, *i.e.*, the intensities of all the spinning sidebands have been added. At sample spinning frequencies greater than 3.8 kHz, the ³¹P CP/MAS spectrum exhibits a single isotropic peak centred at 40.32 ppm. X-ray diffraction experiments indicate that the crystals of 15 are monoclinic with four

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Figure 4.12 Phosphorus-31 CP/MAS spectra of Hg(PPh₃)₂(NO₃)₂ (15) obtained at 4.70 T with MAS frequencies of: (a) 4514, (b) 3831, (c) 2206, (d) 1845 and (e) 1020 Hz.

molecules in the unit cell belonging to the space group C2/c (157). Each molecule has a crystallographic C_2 axis relating the two phosphine ligands and the two nitrate anions, thus the two phosphorus atoms are crystallographically equivalent. The observation of a single peak in the ³¹P MAS spectra at high spinning frequencies confirms the crystallographic equivalence of the two triphenylphosphine ligands. As the spinning frequency decreases, the isotropic peak becomes broader and splits. Further decrease in the MAS frequency causes the intensity of the outer peaks to grow. Simultaneously their separations decrease. In general, a four-line spectrum is observed over the normal range of sample spinning frequencies, *i.e.*, 1.0-4.0 kHz. Moreover, it is clear that this four-line pattern belongs to the unusual *J*-recoupling pattern (type II) as defined in §4.4.1. From the separation of ω_1 and ω_2 as well as that of ω_3 and ω_4 , the value of ${}^2J({}^{31}P, {}^{31}P)$ in 15 was determined to be 250 \pm 10 Hz. This value for ${}^2J({}^{31}P, {}^{31}P)$ is in excellent agreement with the corresponding value found for a related compound, Hg(PMe₃)₂(NO₃)₂, 250 Hz (154).

The ³¹P MAS NMR spectra of **15** obtained at a higher magnetic field, 9.40 T, (shown in Fig.4.13) exhibit essentially the same behaviour as those observed at 4.70 T, except that the peaks are broader. For example, at spinning frequencies greater than 7.0 kHz, the ³¹P NMR spectrum exhibits a single peak centred at 40.32 ppm, again confirming that the two ³¹P nuclei are chemically equivalent. At slower spinning frequencies, a four-line spectrum is also observed.

Eqs. (4.35)-(4.39) predict that, for a given system, the *J*-recoupling patterns obtained at different applied magnetic fields should be coincident, provided that the *G*



Figure 4.13 Phosphorus-31 CP/MAS spectra of $Hg(PPh_3)_2(NO_3)_2$ (15) obtained at 9.40 T with MAS frequencies of (a) 7000, (b) 5200, (c) 4000, (d) 3400, and (e) 2000 Hz.

term in Eq.(4.39) is negligible and that spectra are compared on the basis of reduced sample spinning frequencies, ω_R/ω_0 . In Fig.4.14 the line positions in the ³¹P CP/MAS spectra obtained at 4.70 T are plotted against the actual spinning frequency while for the corresponding line positions at 9.40 T the actual spinning frequencies were scaled by a factor of ¹/₂. The agreement between the two *J*-recoupling patterns is excellent. From the pattern in Fig.4.14, it is also apparent that the frequency differences between alternate lines are always constant, the separation of which equals the *J* coupling constant between the two chemically equivalent phosphorus nuclei in Hg(PPh₃)₂(NO₃)₂. Again, the value of 250 ± 10 Hz for ²*J*(³¹P,³¹P) is also confirmed from the ³¹P CP/MAS spectra obtained at 9.40 T.

Based on Eqs.(4.35)-(4.39), it is clear that, for a given ω_J , the *J*-recoupling patterns can be sufficiently characterized only by the mixing term, *D*. Therefore, instead of showing all four lines in the *J*-recoupling patterns, only the observed and calculated *D* terms are compared; see Fig.4.15. The four line positions can be easily obtained using $\omega_J/2\pi = 250$ Hz and Eqs.(4.35)-(4.39). The effective Hamiltonian includes $\mathcal{H}^{(0)}$, $\mathcal{H}^{(1)}$, $\mathcal{H}^{(2)}$ and $\mathcal{H}^{(3)}$. The agreement between the observed and calculated *D* terms is good in the spinning frequency range of 1.5-4.0 kHz, indicating that the effective Hamiltonian including high-order correction terms up to $\mathcal{H}^{(3)}$ is sufficient to describe the observed MAS NMR spectra in this spinning frequency range. At frequencies below 1.5 kHz the experimental data deviate from the theoretical curve, implying that higher-order correction terms become important for such slow frequencies.



Figure 4.14 The *J*-recoupling patterns observed at 4.70 T (open circles) and 9.40 T (closed circles) in ³¹P MAS NMR spectra of $Hg(PPh_3)_2(NO_3)_2$ (15).



Figure 4.15 Calculated (continuous curve) and observed D terms in the J-recoupled spectra of $Hg(PPh_3)_2(NO_3)_2$ (15) at 4.70 T (open circles) and 9.40 T (closed circles) as a function of scaled sample spinning frequency.

The parameters obtained from the simulation are: $k_1/2\pi = 3.2 \pm 0.8 \times 10^5$ (Hz²), $f_2/2\pi = 5.5 \pm 0.8 \times 10^8$ (Hz³), $g_2/2\pi = 0.0$ (Hz³) and $k_3/2\pi = -3.5 \pm 0.8 \times 10^{11}$ (Hz⁴). These parameters are independent of the applied magnetic field, provided that the scaled sample spinning frequencies are used. It is readily seen from Eqs.(4.28) and (4.29) that the coefficients g_{2n} are small if the difference between the two chemical shift tensors is larger than the direct dipolar coupling. From the ratio of f_2/k_1 , the magnitude of the difference between the two chemical shift tensors can be estimated, *i.e.*, $\Delta/2\pi = f_2/k_1 = 1.7$ kHz. Based on a P-P separation of 4.474 Å obtained from the X-ray diffraction study of 15 (157), the direct dipolar coupling constant was calculated to be 220 Hz, which is indeed much smaller than Δ . Also, the fact that the *J*-recoupling patterns obtained at two different applied magnetic fields become coincident provides further evidence that the g_{2n} terms are negligible. In principle, based on these calculated coefficients, the relative orientations of the two phosphorus chemical shift tensors can be deduced using the structural data obtained from the X-ray diffraction study and the three principle components of the phosphorus chemical shift tensor obtained from the NMR spectrum of a static powder sample.

The relative intensities and lineshapes in the J-recoupled spectra. As noted in §4.4.1, the relative intensity within the J-recoupled spectrum is also sensitive to the sample spinning frequency. This can be seen in the experimental spectra shown in Figs.4.12 and 4.13. Using k_1 , f_2 , g_2 and k_3 values obtained from the above mentioned line-position simulation, the relative intensities of the outer and inner peaks, S, were also calculated using Eqs.(4.35)-(4.39). From Fig.4.16, it is clear that the agreement is good in a spinning frequency range of 1.5-4.0 kHz, indicating that the effective Hamiltonian, including the average Hamiltonian and its first three correction terms, can reproduce the main characteristics of the observed J-recoupled spectra, *i.e.*, both the peak positions and their relative intensities. It is also obvious that, with spinning frequencies below 1.5 kHz, the agreement between calculated and observed relative intensities deteriorates. The inclusion of higher order correction terms would be necessary to reproduce the relative intensities of peaks observed at such slow MAS frequencies.



Figure 4.16 Calculated (continuous curve) and observed relative intensity within the *J*-recoupled spectra of Hg(PPh₃)₂(NO₃)₂ (15) at 4.70 T (open circles) and 9.40 T (closed circles) as a function of scaled sample spinning frequency.

It is of interest to compare the peak positions and the relative intensities of peaks in the *J*-recoupled spectra with AB spectra obtained in solution NMR studies. Consider the usual *J*-recoupled spectrum (type I) as an example. For such systems, it is only necessary to consider the K_1 term because the magnitudes of the *G* and *F* terms are expected to be smaller than K_1 . At the high spinning frequency limit, an A_2 spectrum is observed. As the spinning frequency decreases, a typical AB quartet results. As the spinning frequency continues to decrease, the low and high frequency parts move apart with the outer peaks becoming more intense, *i.e.*, approaching an AX spectrum. It is ſ

known that such changes in AB spectra are associated with an increase in the chemical shift difference between the two strongly J-coupled spins. The appearance of the J-recoupled spectrum can be readily understood by considering the similarity of the mixing term, D, and the corresponding expression in solution NMR, $[\omega_J^2 + (\omega_A - \omega_B)^2]^{1/2}$. Since the K_I term in Eq.(4.39) is analogous to the chemical shift difference term in solution cases, one can think of the K_I term as an effective chemical shift difference. Because this effective chemical shift difference is inversely proportional to the sample spinning frequency, it vanishes at high spinning frequencies, leading to an A₂ spectrum. At slower spinning frequency, the larger the effective chemical shift difference and therefore the less AB character in the resultant J-recoupled spectra.

It was found in the experimental spectra that, although the peak positions and relative intensities are sensitive to the sample spinning frequency, the linewidths of the individual peaks are approximately independent of the sample spinning frequency. This observation indicates that inhomogeneous line broadening due to the orientation dependence of various order correction terms is small, compared with the natural linewidth in the ³¹P MAS NMR spectra of **15**. This observation also provides proof that the approximation of using peak positions and peak intensities instead of the complete lineshapes in the simulations is valid for the present case.

If one neglects the detailed lineshape of the individual peaks in J-recoupled spectra and uses the square root of the second moment of such a four-line spectrum, $M_2^{1/2}$, to describe the "width" of the observed J-recoupled spectrum, then one has

$$M_2^{1/2} = \left[\left(K_1 + K_3 \right)^2 + G_2^2 + F_2^2 \right]^{1/2} \\ = \left[\frac{k_1^2}{\omega_R^2} + \frac{g_2^2 + f_2^2 + 2k_1k_3}{\omega_R^4} + \frac{k_3^2}{\omega_R^6} \right]^{1/2} \approx \frac{k_1}{\omega_R}$$
(4.51)

The above equation predicts a linear relationship between $M_2^{1/2}$ and $1/\omega_R$, provided that high order terms are negligible. In Fig.4.17, the observed $M_2^{1/2}$ was plotted against the sample spinning frequency. Indeed, a linear relationship was found for high spinning frequencies with the initial slope being equal to k_I .



Figure 4.17 Spinning frequency dependence of $M_2^{\frac{1}{2}}$ in the *J*-recoupled spectra of Hg(PPh_3)_2(NO_3)_2 (15) at 4.70 T (open circles) and 9.40 T (closed circles). The initial slope is given by $k_1/2\pi$, 3.2×10^5 (Hz²).

In the early study of ¹³C MAS spectra of solid diammonium oxalate, Maricq and Waugh (104) predicted a $1/\omega_R$ dependence of the linewidth. Recently, Challoner *et al.*

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(112) also observed that the linewidth in the *J*-recoupled spectra of TBPDP increases as the sample spinning frequency is decreased. Levitt *et al.* (125) distinguished between linewidths due to a resonant splitting and inhomogeneous broadening. They demonstrated a different spinning frequency dependence for the ¹³C MAS NMR linewidths of dimethylsulphone-¹³C₂ and 1,2-¹³C₂-glucose. For Hg(PPh₃)₂(NO₃)₂, it was found that the "widths" of the *J*-recoupled spectra exhibit a $1/\omega_R$ dependence at high spinning frequencies. Since the crystallographically equivalent ³¹P spin pair in Hg(PPh₃)₂(NO₃)₂ satisfies an "n = 0 rotational resonance" condition, the "width" of the *J*-recoupled spectra is clearly associated with a resonant splitting as defined by Levitt *et al.* (125). In fact, the inhomogeneous broadenings are negligible in the present case.

In more general cases, inhomogeneous broadening can be large especially in the slow spinning frequency region (55). In the following discussion, only the average Hamiltonian, $\mathcal{H}^{(0)}$, and its first-order correction term, $\mathcal{H}^{(1)}$, are considered for simplicity. Theoretical J-recoupled spectra (type I) as a function of sample spinning frequency are shown in Fig.4.18. Since the first-order correction coefficient, k_I , depends on crystallite orientation in the applied magnetic field, it results in inhomogeneous broadening of individual peaks in J-recoupled spectra of powder samples. It is seen in Fig.4.18 that in addition to changes in the line position, the line shapes of individual peaks show significant broadening at slow spinning frequencies.

2D J-resolved spectra. In order to obtain an independent measurement of ${}^{2}J({}^{31}P,{}^{31}P)$ in 15, 2D ${}^{31}P$ homonuclear J-resolved experiments were performed at 4.70 T under MAS conditions. In the 2D experiments, the t_{I} increments were synchronized



Figure 4.18 Theoretical *J*-recoupled spectra for a pair of crystallographically equivalent spins at MAS frequencies of: (a) 4000, (b) 3000, (c) 2000, and (d) 1000 Hz. The central feature in the spectra shown in (b)-(d) has been cut-off for clarity. The parameters used in the simulations are: $\delta_{11} = 150$, $\delta_{22} = 50$ and $\delta_{33} = 0.0$ ppm; the δ_{33} components of the two chemical shift tensors are coincident; the two δ_{22} components make an angle of 65°; the internuclear vector bisects the angle made by the two δ_{22} components; the dipolar coupling constant, $R_{DD} = 400$ Hz; $\omega_J/2\pi = 200$ Hz; Larmor frequency, 81.03 MHz.

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Figure 4.19 Isotropic (a) and first-order low frequency spinning sideband (b) regions of the 1D ³¹P CP/MAS and 2D ³¹P CP/MAS *J*-resolved spectra of Hg(PPh₃)₂(NO₃)₂ (15) at 4.70 T. The spinning frequency was 1.80 kHz.

with the rotor (138,152). The homonuclear J coupling constant is given by the splitting along the f_1 dimension in the 2D J-resolved spectrum. The contour plot of a homonuclear ³¹P J-resolved spectrum of Hg(PPh₃)₂(NO₃)₂ obtained at a spinning frequency of 1.80 kHz is shown in Fig.4.19. From the 2D spectra, ²J(³¹P,³¹P) = 250 ± 15 Hz, confirming the analysis of the 1D spectra.

It is also apparent from Fig.4.19 that the four-line pattern in the isotropic region is different from that in the first low-frequency spinning sideband. In particular, the two outer lines in the isotropic part are too weak to be seen while the two central lines in the first low-frequency spinning sideband are less intense than the two outer lines. Such a difference in relative intensity within the four-line pattern also manifests itself in the 2D *J*-resolved spectrum. As it has been pointed out in §4.4.1, the effective Hamiltonian derived from the AHT cannot describe features in the spinning sidebands of MAS NMR spectra. Hence, although the *total* MAS NMR spectrum (summed over all spinning sidebands) can be accurately predicted using the effective Hamiltonian in Eq.(4.14), the detailed structure of individual spinning sideband cannot be understood using this effective Hamiltonian. A complete description of spinning sideband structure in the MAS NMR spectra can be obtained using the Floquet theory as demonstrated by Schmidt and Vega (*128*), and Nakai and McDowell (*129*), or from numerical calculations.

Summary. It has been shown that, for a pair of crystallographically equivalent but magnetically non-equivalent spins, the solid-state MAS NMR spectra obtained at slow spinning frequencies exhibit a general four-line spectrum. The J coupling constant, which cannot be measured directly in solution-state NMR spectra or fast MAS NMR

spectra of such a spin pair, can be determined directly from the slow MAS NMR spectra of solid samples. Using average Hamiltonian theory, explicit expressions for the spinning frequency dependence of correction terms to all orders have been derived. All observed spinning-frequency dependent phenomena can be understood on this theoretical basis. The theory predicts three general types of *J*-recoupling patterns. Although the type I and II *J*-recoupling patterns have been observed experimentally, the type III pattern has not yet been reported.

When the J coupling constant involving two crystallographically equivalent spins is small relative to the direct dipolar coupling constant between them, the resultant Jrecoupled spectrum usually exhibits a type I pattern. If the J coupling constant is comparable to the dipolar coupling constant, a type II J-recoupling pattern is possible. Only in systems where the J coupling constant is large and comparable to the slowest spinning frequencies, may the type III J-recoupling pattern be observed.

The theory derived here was successfully applied to analyze the unusual *J*-recoupling patterns (type II) observed in ³¹P CP/MAS spectra of Hg(PPh₃)₂(NO₃)₂. It has been demonstrated that such unusual *J*-recoupling patterns cannot be understood with the average Hamiltonian and its first order correction term alone; instead, higher correction terms must be included. This is the first time that corrections higher than the first-order are found to have significant influences on MAS NMR spectra. By considering the average Hamiltonian and its first three correction terms, the *J*-recoupled spectra of Hg(PPh₃)₂(NO₃)₂ observed at 4.70 T and 9.40 T were well reproduced for sample spinning frequencies in the range of 1.5-4.0 kHz and 3.0-8.0 kHz, respectively.

It is also clear that higher order correction terms are necessary for reproducing the *J*-recoupled spectra at very slow sample spinning frequencies. Analysis of the *J*-recoupling patterns obtained at 4.70 T and 9.40 T yields ${}^{2}J({}^{31}P,{}^{31}P) = 250 \pm 10$ Hz. This value was confirmed by obtaining the 2D ${}^{31}P$ *J*-resolved spectrum. Analysis of the *J*-recoupling pattern arising from a spin pair consisting of two crystallographically equivalent nuclei in the solid state potentially permits one to deduce information concerning the relative orientation of their respective chemical shift tensors.

In analyzing *J*-recoupled MAS NMR spectra from a pair of crystallographically equivalent spins, it is apparent that one must first identify the type of *J*-recoupled spectrum one is dealing with. This can be accomplished by obtaining MAS NMR spectra at a wide range of sample spinning frequencies preferably at two applied magnetic fields. This will assure one of obtaining the correct *J* coupling constant. It is anticipated that *J*-recoupling phenomena can be of general importance in a wide variety of systems containing crystallographically equivalent spin pairs.

4.5 NMR lineshapes arising from a pair of non-equivalent homonuclear spins

In §4.3 it has been shown that, when two spins are slightly non-equivalent and coupled by the dipolar interaction, MAS NMR spectra exhibit spinning-frequency dependent splittings. In this section, attention will be paid to the *linesh*. ²s of NMR resonances in MAS spectra arising from two non-equivalent spins.

4.5.1 Lineshapes in MAS spectra

Since high-order correction terms, G, F and K, are functions depending on orientations of the particular crystallites with respect to the external magnetic field, each of the four NMR resonances given by Eqs.(4.35)-(4.38) will, in fact, describe an NMR resonance with a frequency distribution. Because the intensity of each resonance is also dependent on high-order terms, the resultant NMR resonances will exhibit structures or lineshapes. Furthermore, such MAS lineshapes should be sensitive to the sample spinning frequency.

For simplicity, it is assumed in this section that the average Hamiltonian and its first-order correction are sufficient to describe the MAS spectra. Under this condition, Eqs.(4.35)-(4.39) become:

$$\omega_1 = \frac{1}{2} (\omega_{\Sigma} + D + \omega_J); \qquad P_1 = 1 - \frac{\omega_J}{D}$$
 (4.52)

$$\omega_2 = \frac{1}{2} (\omega_{\Sigma} + D - \omega_J); \qquad P_2 = 1 + \frac{\omega_J}{D}$$
 (4.53)

$$\omega_3 = \frac{1}{2} (\omega_{\Sigma} - D + \omega_J); \qquad P_3 = 1 + \frac{\omega_J}{D}$$
 (4.54)

$$\omega_4 = \frac{1}{2} (\omega_{\Sigma} - D - \omega_J); \qquad P_4 = 1 - \frac{\omega_J}{D}$$
 (4.55)

where

$$D = \left[\omega_{\Delta}^{2} + \omega_{J}^{2} + K_{1}^{2} \right]^{1/2}$$
(4.56)

It is readily seen from Eq.(4.21) that the K_1 term depends on both the dipolar interaction
and the instantaneous chemical shift difference. Since K_I is inversely proportional to the spinning frequency, this leads to significant line broadening under conditions of slow spinning. Also, one may notice from Eqs.(4.52)-(4.56) that the contribution of the K_I term to the observed MAS lineshape depends strongly on the crystallographic equivalence of the two nuclear spins. If the two spins have a large isotropic chemical shift difference, ω_{Δ} , the line broadening due to K_I is minimized (except under conditions of rotational resonance); however, additional shifts in the line positions may still be observable (108). If the two spins are magnetically equivalent, the K_I term vanishes. If the two spins are crystallographically equivalent but magnetically non-equivalent, the K_I term causes splittings and line broadening as discussed in §4.4.

4.5.2 Results and discussion

As mentioned in §3.5.1, the results of an X-ray diffraction study show that the crystals of *cis*-azobenzene-¹⁵N₂ dioxide (10) are orthorhombic (space group P*bcn*) with eight molecules in the unit cell and one complete molecule in the asymmetric unit (86). The ¹⁵N CP/MAS spectra of 10 were obtained over a spinning frequency range of 1.2 to 6.0 kHz at B₀ = 4.70 T. Typical ¹⁵N MAS spectra of 10 are shown in Fig.4.20. Two symmetrical isotropic peaks at 311.1 and 308.9 ppm were observed at spinning frequencies higher than 5.5 kHz. This indicates that the two ¹⁵N nuclei in 10 are slightly non-equivalent, which is consistent with the X-ray diffraction study (86). The isotropic ¹⁵N chemical shift difference in 10 was also confirmed by obtaining the ¹⁵N CP/MAS spectra



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Figure 4.20 Nitrogen-15 MAS NMR spectra of cis-azobenzene-¹⁵N₂ dioxide (10) obtained at 4.70 T as a function of the sample spinning frequency.

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as a function of sample spinning frequency are threefold. (*i*) At spinning frequencies less than the span of the chemical shift tensor (in frequency units), a number of spinning sidebands become evident. At any given spinning frequency the detailed lineshapes of different order spinning sidebands differ. (*ii*) As the spinning rate decreases, the splitting of the doublet increases. For example, at a spinning frequency of 6.0 kHz the splitting of the doublet is about 46 Hz while at 1.2 kHz it increases to about 86 Hz. (*iii*) The most interesting change is that the doublet broadens at slower spinning frequencies and distortions due to the appearance of outer shoulders become significant at spinning frequencies less than 1.2 kHz.

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Since the average Hamiltonian describes only the "total MAS spectra" (104), it is necessary to sum all spinning sidebands so that the total observed lineshapes can be compared with those calculated using Eqs.(4.52)-(4.56). The observed MAS lineshapes of **10** (sum over all spinning sidebands) as a function of spinning frequency are shown in Fig.4.21. At the high spinning frequency limit of 6.0 kHz, the MAS spectrum shows two sharp isotropic peaks. At slower spinning rates the separation of the peaks increases and the peaks broaden systematically with decreasing spinning speed. As has been pointed out in §4.5.1, the detailed MAS lineshapes shown in Fig.4.21 depend on the magnitude and orientation of the ¹⁵N chemical shift tensors with respect to the ¹⁵N-¹⁵N dipolar vector. Therefore, before the MAS lineshape for a specific system can be calculated, it is necessary to characterize the orientations of the chemical shift tensors. Fortunately, the nitrogen chemical shift tensors in **10** have been characterized in §3.5.1 from an analysis of the static NMR spectra.



Figure 4.21 The observed (a) and calculated (b) total MAS lineshapes of *cis*azobenzene- $^{15}N_2$ dioxide (10) obtained at 4.70 T as a function of sample spinning frequency.

Since the homonuclear dipolar interaction between the two ¹⁵N nuclei in **10** is homogeneous, the line broadening cannot be completely removed by MAS due to the non-coincidence of the large anisotropic nitrogen chemical shift tensors. Because there is an approximate $C_{2\nu}$ symmetry about the CN(O)-N(O)C moiety in **10**, a coordinate system suitable to such symmetry is chosen, which is also the principal axis system for the ¹⁵N-¹⁵N dipolar interaction. Under these conditions, it can be shown that the K_I term has the following form:

$$K_{1} = \left(\frac{\pi R_{DD}}{6\omega_{R}}\right)\omega_{0}(\delta_{11} - \delta_{22})\sin 2\phi_{22} (7\cos^{2}\theta + 1)\sin\theta\sin\phi \qquad (4.57)$$

where ϕ_{22} is the angle between δ_{22} and the dipolar vector and the angles θ and ϕ orient the dipolar vector with respect to the applied magnetic field.

It is clear from Eq.(4.57) that the line broadening in MAS spectra is proportional to the product of the dipolar coupling constant and the largest instantaneous chemical shift difference, $(\delta_{11} - \delta_{22})\sin 2\phi_{22}$. From the two nitrogen chemical shift tensors in 10, it is easy to show that this largest instantaneous chemical shift difference corresponds to situations where the applied magnetic field lies in the N(O)-N(O) plane and makes an angle of 45° with respect to the N-N bond. Although the dipolar coupling constant, 540 Hz, is relatively small compared with the spinning frequency of several kilohertz, the largest instantaneous chemical shift difference, 2.6 kHz at B₀ = 4.70 T, makes the K_1 term of Eq.(4.56) significant. In spite of the fact that the experimentalist has no control over the angle ϕ_{22} in any given system such as 10, it is still interesting to note that K_1 vanishes at $\phi_{22} = 0^\circ$ and 90°, since under either of these conditions the two chemical shift tensors become coincident.

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The MAS lineshapes calculated using Eqs.(4.52)-(4.56) are compared with those observed; see Fig.4.21. Since the two nitrogen chemical shift tensors and the dipolar coupling constant have been determined from the analysis of the static lineshape, the only other parameter that can be adjusted to possibly improve the fit is ${}^{1}J({}^{15}N,{}^{15}N)$. Here, J was taken to be 10 Hz for the simulated spectra shown in Fig. 4.21; however, it was found that the simulated MAS lineshapes were not sensitive to ${}^{1}J({}^{15}N,{}^{15}N) < 10$ Hz. A small value for this coupling constant agrees with previous general observations (158). The fact that only two isotropic peaks (the half-height line width is less than 25 Hz) are observed at the high spinning limit, 6.0 kHz, also confirms that ${}^{1}J({}^{15}N, {}^{15}N)$ is small. It is clear from Fig.4.21 that the simulated MAS lineshapes reproduce the observed ones reasonably well over a large range of sample spinning frequencies, indicating that the average Hamiltonian and its first-order correction are sufficient to describe the ¹⁵N MAS NMR lineshapes in 10. However, it is also noticed that, at the low spinning frequency limit of 1.2 kHz, the simulated MAS lineshape tends to exceed the observed line width. This discrepancy may suggest a critical region where higher order correction terms start to contribute to the MAS lineshape.

Another interesting aspect of the MAS lineshape is its field dependence. A higher applied magnetic field enhances the instantaneous resonance frequency difference between the nuclei under investigation, and therefore enhances the line broadening. It was found that at 9.40 T both the splitting and the line broadening in the MAS spectra of 10 were approximately doubled in frequency units compared with those observed at 4.70 T.

However, the overall MAS lineshape possesses essentially the same features at the two different fields. In §4.3.2 it was pointed out that a higher field tends to quench the spinning-frequency dependence of the MAS spectra for two non-equivalent spins. In the case of 10, since ω_{Δ} (45 Hz at 4.70 T) is small compared with K_I (ca. 500 Hz at 4.70 T), K_I dominates the mixing term D. Therefore, the change of an applied magnetic field from 4.70 to 9.40 T is not significant enough to result in any observable quenching effect. This is consistent with the prediction from Eqs.(4.52)-(4.56), provided that the J coupling constant is small compared with the isotropic chemical shift difference.

In a recent study, Nakai and McDowell systematically investigated the ¹³C MAS lineshapes in sodium acetate-¹³C₂ as a function of spinning frequency (*129*). In addition to significant rotational resonance effects, they observed that under non-rotational resonance conditions the centre of gravity of the ¹³C MAS lineshape not only shifted with respect to the isotropic chemical shift, but also was dependent on spinning rate. In the case of **10**, similar observations were made, but the dependence of the centre of gravity of the ¹⁵N MAS lineshape as a function of spinning frequency is different from their case. In contrast to the observation in sodium acetate-¹³C₂ that the additional shifts monotonically increase with the spinning frequency, the additional shifts in **10** were found to decrease as the spinning frequency part of the ¹⁵N MAS lineshape shifts to high frequency as the spinning frequency is increased while the high frequency part of the MAS lineshape shifts equally in the opposite direction. The observed separation between the two mass centres in the MAS spectra equals the isotropic chemical shift difference

at the high spinning limit of 6.0 kHz while, at slow spinning frequencies, it is always greater than the isotropic chemical shift difference. Because of the large isotropic chemical shift difference in sodium acetate- ${}^{13}C_2$ ($\omega_{\Delta}/2\pi = 7839$ Hz at 4.70 T), it is only practical to study the ^{13}C MAS lineshape at spinning frequencies on the order of $\omega_{\Delta}.$ In the case of 10, however, the isotropic chemical shift difference of the two non-equivalent ^{15}N nuclei is very small ($\omega_{\Delta}/2\pi$ = 45 Hz at 4.70 T) and the spinning frequencies are much greater than ω_{Λ} . It is probably this difference in relative spinning rates with respect to ω_{Δ} that is responsible for the different behaviour observed for the mass centre of the MAS lineshape in sodium acetate- ${}^{13}C_2$ and 10. The observed separation of the two "mass centres" of the ¹⁵N MAS lineshape in **10** as a function of spinning frequency is shown in Fig.4.22. Since the J coupling constant is found to be small, the four transitions given in Eqs.(4.52)-(4.56) can be reduced to two for simplicity. In such a case, the "mass centres" for the two transitions appear at $1/2(\omega_{\Sigma}\pm <\!D\!>$) and the separation between them equals $\langle D \rangle$. It is readily shown that such a separation, if defined as Δ' , has the following limit:

$$\lim_{\omega_R \to \infty} \Delta' = \lim_{\omega_R \to \infty} \langle D \rangle = \omega_{\Delta}$$

$$(4.58)$$

Eq. (4.57) indicates that, at the high spinning frequency limit, the separation between the observed peaks equals the isotropic chemical shift difference of the two non-equivalent spins. The theoretical curve describing the separation between the "mass centres" in the MAS spectra is calculated using Eqs. (4.52)-(4.56) and is also shown in Fig. 4.22. It is readily seen that the agreement is good. This curve clearly shows that, as the sample

spinning frequency increases, the separation between the two "mass centres" approaches the isotropic chemical shift difference in frequency units, 45 Hz. As predicted in §4.3.2, with higher magnetic fields, the separation between the two "mass centres" of the



Figure 4.22 Observed (filled circles) and calculated (solid curve) separation, Δ' , between the two "mass centres" in the ¹⁵N MAS lineshape of *cis*-azobenzene-¹⁵N₂ dioxide (10) obtained at 4.70 T as a function of the sample spinning frequency. The small irregular oscillations in the calculated curve are due to the small number of points used in the powder averaging.

individual lineshape will be increased in frequency units. However, the isotropic chemical shift difference is so small in 10, it is expected that a curve similar to that shown in Fig.4.22 will be observed at 9.40 T.

Because only the first-order correction is included in theoretical calculations on MAS lineshapes, this indicates that the Magnus expansion series converges rapidly in the case of **10**. In §4.2.2, spinning frequency limits for a converged Magnus expansion series were discussed using **10** as an example. The convergence limit derived by applying Maricq's expression to a particular crystallite is approximately 1.5 kHz. From Fig.4.21 and 4.22, it is clear that this spinning frequency limit is reasonable.

In summary, the two ¹⁵N nuclei in **10** are found to be slightly non-equivalent in the solid state. The "total" MAS lineshape resulting from such a spin pair is shown to be sensitive to the spinning frequency. With the knowledge of the ¹⁵N chemical shift tensors, the homonuclear dipolar interaction and their mutual orientations in the molecule, the detailed MAS lineshape in **10** can be well characterized over a large range of spinning frequencies by considering the first-order correction term to the average Hamiltonian. Such a spinning-frequency dependent lineshape is a direct consequence of homonuclear dipolar coupling and the orientation dependent chemical shift difference. Although the two nuclear spins are non-equivalent and the mutual dipolar interaction is small, the line broadening is still significant when the MAS frequency is smaller than the instantaneous chemical shift difference (in Hz) of the nuclei under study. Therefore, it is believed that, in similar systems with larger chemical shift anisotropies, the MAS line broadening could be severe.

4.6 MAS NMR spectra of second-order two-spin systems

In the previous three sections, §4.3, §4.4 and §4.5, MAS NMR spectra of several

special cases have been studied. In this section, more general second-order (tightly *J*-coupled) two-spin systems will be examined.

4.6.1 Spinning-frequency dependence of second-order MAS NMR spectra

It is interesting to note that at the rapid spinning extreme, *i.e.*, when the terms K, G and F approach zero, Eqs.(4.35)-(4.39) are identical with those used to describe AB spin systems in solution state NMR studies. Under conditions of slow spinning, however, the second-order MAS NMR spectra deviate significantly from their solution-state counterparts. In this section attention will be focused on the spinning-frequency dependence of peak positions and relative intensities in the second-order MAS NMR spectra.

As mentioned in §4 3 and §4.4, the G terms are usually much smaller than other correction terms and therefore can be neglected. In such cases, Eq.(4.39) can be simplified to:

$$D = \left[\omega_{\Delta}^{2} + (\omega_{J} - F)^{2} + K^{2} \right]^{1/2}$$
(4.59)

In a manner similar to that for AB spectra in solution NMR studies, the appearance of second-order features in MAS NMR studies of solids is also dependent on the magnitude of the mixing term, D. It is convenient to define a quantity, $D_{+\infty}$, as:

$$D_{+\infty} = \lim_{\omega_R \to +\infty} D(\omega_R) = (\omega_{\Delta}^2 + \omega_J^2)^{1/2}$$
(4.60)

Analogous to the discussion on J-recoupling patterns in §4.4.1, three general

types of spinning-frequency dependent behaviour for second-order MAS NMR spectra can be also identified, depending on the relative magnitudes of D and $D_{+\infty}$. The three general cases are: (I) $D(\omega_R) = D_{+\infty}$, (II) $D(\omega_R) > D_{+\infty}$ and (III) $D(\omega_R) < D_{+\infty}$. The characteristic spinning-frequency dependence of D for each of these situations is illustrated in Fig.4.23. It is clear that not only are the relative magnitudes of D different in each of these three cases, but also the way in which D depends on the MAS spinningfrequency is distinctive. These three types of MAS NMR spectra will be discussed in more detail.



Figure 4.23 A schematic diagram illustrating the spinning-frequency dependence of D in all three types of MAS NMR spectra for AB spin pairs.

In systems that exhibit type I behaviour, the mixing term, D, is *independent* of the sample spinning frequency and always equals $D_{+\infty}$; the peak positions of the MAS NMR spectra do not change as the sample spinning frequency is varied. Also, the peak positions are predicted to be identical with those derived for AB spectra in isotropic fluids (solutions). This type of behaviour will most frequently arise when the isotropic chemical shift difference is relatively large compared to the various correction terms appearing in Eq.(4.39). From Eq.(4.39) it is obvious that a large value of ω_{Δ} will tend to quench the spinning-frequency dependence of D. However, even with large values of ω_{Δ} , the relative intensities of the peaks within the four-peak pattern may still be sensitive to the sample spinning frequency if the term F is comparable to ω_J (see Eqs.(4.35)-(4.39)).

For spin systems which exhibit type II behaviour, $D > D_{+\infty}$ under slow spinning conditions; the general appearance of the second-order MAS NMR spectra is analogous to that of solution AB spectra in the sense that the splittings between the adjacent outer peaks in the four-peak pattern equals ω_J . As the sample spinning frequency increases, the *D* term decreases and approaches $D_{+\infty}$. The ¹⁵N MAS NMR spectra of *cis*azobenzene-¹⁵N₂ dioxide shown in §4.5.2 provide an example of this type of spin system. Challoner and McDowell also predicted this type of spinning frequency dependence for the AB portion of an ABX spin system (139).

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For the third case (type III), where $D < D_{+\infty}$, the four peaks in the MAS spectrum are "squeezed" compared with those that would be observed in analogous solution-state AB NMR spectra. In contrast to the type II MAS NMR spectra, the D

term in the type III MAS NMR spectra increases as the sample spinning frequency is increased. Since anomalous spectral features may be observed for the type III spin systems the discussion which follows is focused on these systems.

As has been pointed out in §4.4, the relative magnitude of D and ω_J has a profound influence on the appearance of MAS NMR spectra. For any given AB spin system, there are three general spinning-frequency regions where the following conditions may be satisfied: (i) $D > \omega_I$, (ii) $D = \omega_I$ and (iii) $D < \omega_I$. In these three regions, MAS NMR spectra will have distinct features, as illustrated in Fig.4.24. It is interesting to note that when D is greater than ω_J , the MAS NMR spectra are normal in the sense that ω_1 is given by the splittings between the adjacent outer peaks (Fig.4.23(a)). However, a triplet results when D equals ω_J (Fig.4.24(b)). When D becomes smaller than ω_J , an interchange of the two inner peaks results in an unusual AB spectrum since ω_J is given by the separation between alternate peaks (Fig.4.24(c)). Similar unusual AB spectra have been previously observed for systems containing two crystallographically equivalent spins (115). In order to extract ω_J from MAS spectra of strongly coupled two-spin systems in solids, one must carefully examine the spinning-frequency dependence of the peak positions so that the relative magnitudes of D and ω_I can be determined. It should be pointed out that Eqs.(4.35)-(4.39) are similar to the expressions derived by Challoner and McDowell (139) considering the average Hamiltonian and its first-order correction. However, their expressions can predict only the type II behaviour. Clearly, correction terms higher than first order are necessary to predict MAS NMR spectra of type I and III.



Figure 4.24 A schematic diagram illustrating the distinct appearance of second-order MAS NMR spectra (type III) in three regions: (a) $D > \omega_J$, (b) $D = \omega_J$ and (c) $D < \omega_J$. Note that the two inner peaks interchange their relative positions on going from (a) to (c).

Eqs.(4.35)-(4.39) indicate that for all three types of MAS spectra, the relative intensities within the four-peak pattern depend strongly on the sample spinning frequency. This is in contrast to MAS spectra of AX spin systems (159). For AB spin systems the relative intensities of the four peak pattern may depend on the spinning frequency in a complex manner varying from system to system. Nevertheless, some general trends are worth mentioning at this stage. Eqs.(4.35)-(4.39) predict that under slow MAS conditions, the intensity ratio (S), which is defined as the intensity of the outer peaks over that of the inner peaks, is usually greater than that predicted using formulae appropriate for solution-state NMR studies. In other words, less "AB character" will be observed in MAS NMR spectra of AB spin systems under slow MAS conditions. The slower the sample spinning frequency, the *istention* frequency, the *istention* system of AB spin systems under slow MAS conditions. The slower the sample spinning frequency is soft as the intensity ratio, S. More specific discussions regarding the relative intensities of peaks in MAS NMR spectra of AB spin systems will be given in the next section (§4.6.2).

§4.6.2 Results and discussion

MAS NMR spectra of the Type III. The four ³¹P nuclei present in the phosphole

tetramer (16) can be treated as two "isolated" spin pairs. The dipolar and J coupling constants between the two directly-bonded ³¹P nuclei are much greater than the other ${}^{31}P{}^{-31}P$ interactions. Based on the crystal structure of a molybdenum carbonyl complex of 16 (160),



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the two ³¹P spin pairs in 16 are believed to be related by an approximate C_2 symmetry axis. Observation of only one AB spectrum also supports the argument that the two ³¹P spin pairs in the molecule are symmetrically related. In Fig.4.25 the ³¹P MAS NMR spectra of 16 obtained at 4.7 T are shown as a function of the sample spinning frequency. Note that each spectrum represents the *total* lineshape of the corresponding



Figure 4.25 Observed total ³¹P MAS NMR spectra of the phosphole tetramer, 16, at 4.70 T with different sample spinning frequencies.

MAS NMR spectrum, *i.e.*, a spectrum summed over all spinning sidebands. The ^{31}P MAS NMR spectrum of 16 appears as a triplet at all spinning frequencies. The central peak consists of two overlapping peaks that are too close to be resolved (vide infra). A plot of the separation between the two outer peaks, $(D+\omega_J)$, against ω_R is shown in Fig.4.26. The ³¹P MAS NMR spectra of 16 obtained at a higher applied magnetic field, 9.4 T, also exhibit triplet structures similar to those obtained at 4.7 T. The separation between the two outer peaks for spectra at 9.4 T is also plotted as a function of sample spinning frequency in Fig.4.26. Note that for data obtained at 9.4 T, the sample spinning frequency is scaled by a factor of $\frac{1}{2}$, which is the ratio of ^{31}P NMR Larmor frequencies at the two fields. It can be easily shown from Eqs.(4.35)-(4.38) that the separation between the outer peaks equals $(D+\omega_I)$ irrespective of relative values of $D(\omega_R)$ and $D_{+\infty}$. Also, at the high spinning frequency limit, this separation approaches ($D_{+\infty}$) $+ \omega_1$). From Fig.4.26 it is clear that the ³¹P spin pair in 16 exhibits the type III behaviour of spinning-frequency dependence, as defined in §4.6.1. By including only the first three correction terms in Eq.(4.59), and omitting the term containing $(1/\omega_R)^6$, the mixing term, D, can be approximated by Eq.(4.61).

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$$D = \left[\omega_{\Delta}^{2} + \left(\omega_{J} - \frac{f_{2}}{\omega_{R}^{2}} \right)^{2} + \left(\frac{k_{1}}{\omega_{R}} + \frac{k_{3}}{\omega_{R}^{3}} \right)^{2} \right]^{1/2}$$

$$\approx \left[\omega_{\Delta}^{2} + \omega_{J}^{2} + \frac{k_{1}^{2} - 2\omega_{J}f_{2}}{\omega_{R}^{2}} + \frac{f_{2}^{2} + 2k_{1}k_{3}}{\omega_{R}^{4}} \right]^{1/2}$$

$$(4.61)$$

From Fig.4.26 it is clear that $(D+\omega_J)$ is nearly independent of sample spinning

frequencies greater than 3 kHz. This indicates that in the case of 16 the correction



Figure 4.26 Calculated (solid curves) and observed separation between the two outer peaks in the ³¹P MAS NMR spectra of the phosphole tetramer, **16**, at 4.70 T (open circles) and 9.40 T (closed circles). The calculated curves are based on Eq.(4.61) using the following parameters: $\omega_{\Delta}/\omega_0 = 1.73$ ppm, $\omega_J / 2\pi = 362$ Hz and $f_2^2 + 2k_J k_3 = -(2\pi)^6 \times 0.9$ (kHz⁶).

term(s) containing $(1/\omega_R)^2$ must be very small or zero. Indeed, simulated results including only the $(1/\omega_R)^4$ correction term agree well with the observed data. From the value of $D_{+\infty}$ obtained at two fields, both ω_{Δ} and ω_J can be accurately determined.

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Analysis yields $\omega_{\Delta}/\omega_0 = 1.73$ ppm and $\omega_J/2\pi = 362$ Hz. These values cannot be directly extracted from MAS NMR spectra obtained at one field since the two inner peaks are not resolved. Based on the above values of ω_{Δ} and ω_J , the separation between the two inner peaks in the ³¹P MAS NMR spectrum obtained with $\omega_R/2\pi = 6.0$ kHz can be calculated as only 0.32 ppm at 4.70 T.

It is interesting to point out that $(D + \omega_J)$ is greater than $2\omega_J$ when $\omega_R/2\pi > 2.5$ kHz and that it becomes smaller than $2\omega_J$ when $\omega_R/2\pi < 2$ kHz (Fig.4.26). Although the two inner peaks in the MAS NMR spectra are not resolved, it is clear that an interchange of the two inner peaks must occur at $\omega_R/2\pi \approx 2$ kHz. Thus, in the case of compound 16, each of the three different regimes depicted in Fig.4.24 can be realized in practice.

Another surprising feature of the MAS NMR spectra shown in Fig.4.25 is that, as the spinning frequency is decreased, the relative intensities of the peaks change dramatically. From Eqs.(4.35)-(4.38) the relative intensity, S, of the outer peaks to the inner peaks is given by Eq.(4.62).

$$S = \frac{D - (\omega_J - F)}{D + (\omega_J - F)}$$
(4.62)

One can easily show that

$$\left(\frac{1-S}{1+S}\right) D = \omega_J - F = \omega_J - \frac{f_2}{\omega_R^2} - \frac{f_4}{\omega_R^4} - \dots$$
(4.63)

All coefficients of k_{2n+1} (n = 0, 1, 2...) and f_{2n} (n = 1, 2, ...) are field-independent, provided that a scaled spinning frequency is used. Eq. (4.63) predicts that for a given AB spin system, a plot of (1 - S)D/(1 + S) vs. the scaled sample spinning frequency will be independent of the applied magnetic field. Indeed, as shown in Fig.4.27, the two curves obtained at different magnetic fields are nearly coincident. The ordinate intercept of the curve confirms the value of $\omega_J/2\pi$, 362 Hz, and the initial slope of the curve yields the value of $f_2/(2\pi)^3$, 3.1 (kHz³). Therefore, given that $k_1^2 - 2\omega_J f_2 = 0$ and $f_2^2 + 2k_1k_3 =$ $-(2\pi)^6 \times 0.9$ (kHz⁶) (see Fig.4.26 and Eq.(4.59)), $k_1/(2\pi)^2$ and $k_3/(2\pi)^4$ are estimated to be 1.5 (kHz²) and -3.5 (kHz⁴), respectively. It is worth noting that one is able to use the same set of *field-independent* correction coefficients, *i.e.*, k_1 , f_2 and k_3 , to reproduce



Figure 4.27 Plot of (1-S)D/(1+S) versus $(\omega_R^{scaled})^{-2}$ in ³¹P MAS NMR spectra of the phosphole tetramer (16) at 4.70 T (open circles) and 9.40 T (closed circles). The initial slope yields $f_2 = (2\pi)^3 \times 3.1$ (kHz³) and the ordinate intercept equals $\omega_1/2\pi$, 362 Hz.

data obtained at two fields, provided that scaled spinning frequencies are used. This indicates that various correction coefficients in the G term are indeed negligible since they are expected to be field-dependent. Only in spin systems where the chemical shift anisotropy is smaller than or comparable to the dipolar coupling constant may the G term be significant.

Surprisingly, at very slow spinning frequencies, *S* becomes greater than unity. This indicates that the outer peaks become more intense than the inner ones. Similar AB spectra have only been observed in single-crystal NMR spectra of diammonium oxalate monohydrate when the crystallite is at some special orientations with respect to the external field (78). This phenomenon can never be observed in AB spectra of solution NMR studies.

MAS NMR spectra of the Type I. In the solid state, the two *cis*-phosphorus atoms of *cis*-1,2-bis(diphenylphosphino)ethylene (17) are slightly non-equivalent (*161*). The direct ³¹P-³¹P dipolar coupling constant is about 430 Hz, based on an estimate of the P-P internuclear distance, 3.57 Å. The ³¹P MAS NMR spectra of 17 obtained at 4.7 T are shown in Fig.4.28. Clearly, only at high MAS frequencies do the MAS NMR spectra of 17 resemble AB spectra predicted by formulae applicable to solution-state NMR studies. It is more astonishing to observe that at slow MAS frequencies, the peak intensities vary drastically from spinning sideband to spinning sideband, and they are sensitive to the MAS frequency at which the spectrum is obtained. The observed anomalous features at individual spinning sidebands cannot be understood using our approach. However, our method is appropriate to treat *total* MAS NMR spectra. The



Figure 4.28 Observed ³¹P MAS NMR spectra of *cis*-1,2-bis(diphenylphosphino)ethylene (17) at 4.70 T with different sample spinning frequencies.

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total MAS NMR spectra of each of the MAS spectra in Fig.4.28 are shown in Fig.4.29. Here, as expected, the anomalous features observed at individual spinning sidebands disappear in the total MAS NMR spectra and symmetrical spectra are always obtained.



Figure 4.29 Observed total ³¹P MAS NMR spectra of *cis*-1,2-bis(diphenylphosphino)ethylene (17) at 4.70 T with different sample spinning frequencies.

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First, one may notice in Fig.4.29 that the peak positions do not change as the sample spinning frequency is varied from 1.0 kHz to 4.5 kHz, in contrast to the observations made for 16. Clearly, the MAS NMR spectra of 17 belong to the type I spin system where $D(\omega_R) = D_{+\infty}$ as discussed previously in §4.6.1. In Fig.4.30 the observed D values in MAS spectra of 17 are plotted versus the sample spinning frequency and indeed a horizontal straight line is obtained. With the knowledge of $\omega_J/2\pi$, which is determined to be 122 Hz, and $D/2\pi = 256$ Hz, one can determine that $\omega_{\Delta}/\omega_0 = 2.78$ ppm.



Figure 4.30 Plot of $D/2\pi$ versus $\omega_R/2\pi$ for ³¹P MAS NMR spectra of *cis*-1,2bis(diphenylphosphino)ethylene (17) obtained at 4.70 T.

A more interesting feature of the total MAS NMR spectra of 17 is that the relative intensities of the peaks vary with the MAS frequency (see Fig.4.29). At the highest MAS frequency, 4.5 kHz, the relative intensity, S = 0.39, compares well with that

calculated based on solution NMR formulae, 0.35. Similar to the MAS NMR spectra of 16, the outer peaks in the AB spectra become more intense as the MAS frequency is decreased. When the spinning frequency is as low as 834 Hz, the MAS spectrum of 17 appears similar to that predicted for an AX spin system, *i.e.*, $S \approx 1$. From Eqs.(4.35)-(4.38) it is clear that the spinning-frequency dependence of relative intensities is sensitive to parameters such as the ³¹P-³¹P dipolar coupling constant, the principal components of the phosphorus chemical shift tensors and their relative orientations with respect to ³¹P-³¹P dipolar vector.

Since the *D* term is constant over the entire spinning-frequency range, the relative intensity *S* depends only on the even-order correction terms, f_{2n} , as indicated by Eqs.(4.35)-(4.38). Here it provides one with an ideal case where the convergence of the high-order correction terms as a function of spinning frequency can be readily investigated. In Fig.4.31 observed relative intensities are compared with those calculated based on Eqs.(4.35)-(4.38) and Eq.(4.59). It is apparent that inclusion of only the second-order correction term, f_2 , provides a reasonable description of the observed intensities when $\omega_R/2\pi$ is above 3 kHz. A further addition of the fourth-order correction term, f_4 , reproduces the observed data over a larger frequency range, $\omega_R/2\pi > 2.0$ kHz. At very slow MAS frequencies, inclusion of f_6 and f_8 can reproduce the observed trend, but the agreement is not good.

In summary, it has been shown that both the frequencies and relative intensities of peaks in MAS NMR spectra of second-order AB spin systems will generally be sensitive to the sample spinning frequency. At the high MAS frequency extreme, MAS



Figure 4.31 Observed (closed squares) and calculated (solid curves) relative intensities in ³¹P MAS NMR spectra of *cis*-1,2-bis(diphenylphosphino)ethylene (17) as a function of sample spinning frequency. Curve (a) includes f_2 ; curve (b) includes f_2 and f_4 ; curve (c) includes f_2 , f_4 , f_6 and f_8 . Parameters used in the calculations are: $f_2 = (2\pi)^3 \times 0.41$ (kHz³), $f_4 = -(2\pi)^5 \times 0.63$ (kHz⁵), $f_6 = (2\pi)^7 \times 0.42$ (kHz⁷) and $f_8 = -(2\pi)^9 \times 0.11$ (kHz⁹). The horizontal line indicates S = 0.35, which is the value obtained from solution formulae.

NMR spectra are identical to the AB spectra predicted by solution NMR formulae. Under slow MAS conditions, however, MAS NMR spectra of AB systems deviate considerably from those predicted using solution-state formulae. Three general types of MAS NMR spectra for AB spin systems can be identified depending on the relative values of $D(\omega_R)$ and $D_{+\infty}$. It is also shown that, if the high-frequency limit cannot be reached in practice, caution must be exercised when extracting parameters (e.g., ω_{Δ} and ω_J) from MAS NMR spectra. It is important to first identify the type of spin system that one is dealing with, *i.e.*, the relative magnitudes of $D(\omega_R)$ and $D_{+\infty}$, so that the MAS spectra can be properly analyzed. It is obvious that a detailed study of MAS NMR spectra as a function of sample spinning frequency will be helpful in this regard. In general, type I behaviour may be anticipated for two-spin systems where the isotropic chemical-shift difference, ω_{Δ} , is larger than or comparable to the dipolar coupling constant between the two spins, R, and ω_J is relatively small. When ω_{Δ} is comparable to R and ω_J , the two-spin system may exhibit type II behaviour. For cases where ω_{Δ} is smaller than R and ω_J , type III behaviour may be expected.

It has been demonstrated that high-order correction terms to the average Hamiltonian play an important role in determining spinning-frequency dependencies of second-order MAS NMR spectra. In particular, correction terms higher than first order are essential to interpret the observed anomalous spinning-frequency dependence in the ³¹P MAS NMR spectra, *e.g.*, unusual *J*-recoupled MAS spectra. The limitation of the current approach is that a rapid convergence of the Magnus expansion series in the effective Hamiltonian is not always guaranteed, especially at very slow MAS frequencies. However, it appears that, in practice, inclusion of the first three correction terms is usually sufficient to reproduce the main features observed in the MAS NMR spectra of AB spin systems.

4.7 Experimental

Bis(methyldiphenylphosphine)(1,5-cyclooctadiene)iridium(I) hexafluorophosphate (13) and *cis*-dichlorobis(triethylphosphine)platinum(II) (14) were obtained from Aldrich Chemical Company and used without further purification. The samples of *cis*azobenzene-¹⁵N₂ dioxide (10) and Hg(PPh₃)₂(NO₃)₂ (15) were kindly prepared by Michael D. Lumsden. The phosphole tetramer (16) was a generous gift from Professor F. Mathey and Professor F. Laporte (*160*). The sample of *cis*-1,2-bis(diphenylphosphino)ethylene (17) was obtained from Strem Chemicals, Inc. and was used without further purification.

All ³¹P MAS NMR spectra were recorded on Bruker MSL-200 (B₀ = 4.70 T) and Bruker AMX-400 (B₀ = 9.40 T) NMR spectrometers operating at ³¹P NMR frequencies of 81.0 and 162.0 MHz, respectively. The crystalline samples were packed into zirconium oxide rotors, 7 mm o.d. and 4 mm o.d., for the low and high field NMR experiments, respectively. Cross polarization (CP) from protons to ³¹P nuclei under the Hartmann-Hahn match condition and high-power proton decoupling were employed for the acquisition of all ³¹P MAS NMR spectra. Typical ¹H 90° pulses were 4.0-5.0 μ s for the low field experiments and 3.5-4.0 μ s for the high field NMR experiments. Contact times of 3-5 ms were used for experiments at both fields. Typical recycle times were between 10 and 60 s. The sample spinning frequency ranged from 1.0 to 6.5 kHz at 4.70 T and 1.5 to 14.0 kHz at 9.40 T. The sample spinning frequency was controlled by Bruker MAS pneumatic units and was stable within ± 2 Hz during all ³¹P MAS NMR $H_3PO_4(aq)$ by setting the ³¹P NMR peak of solid $NH_4H_2PO_4$ to 0.81 ppm.

The solid-state ³¹P 2D J-resolved experiments were performed for 15 at 4.70 T under the condition of CP/MAS. The t_1 increments were synchronized with the rotor, *i.e.*, $t_1 = 2nT_R$. A simple eight-step phase cycling (138) was used. All 2D spectra were acquired in the magnitude mode.

Carbon-13 CP/MAS and dipolar-dephased (nonquaternary carbon suppression) experiments (*162*) were performed for 13 on the Bruker MSL-200 spectrometer operating at 50.32 MHz for ¹³C nuclei. Carbon-13 CP/MAS spectra were referenced with respect to TMS by using solid adamantane as a secondary reference sample. In the dipolar-dephased ¹³C experiments, a dephasing delay of 40 μ s was used.

All ¹⁵N MAS NMR spectra of **10** were obtained on Bruker MSL-200 and AMX 400 spectrometers operating at 20.3 and 40.6 MHz, respectively. Solid-state ¹⁵N NMR spectra were referenced to $NH_3(l)$ by setting the ¹⁵N NMR peak of solid ¹⁵NH₄NO₃ to 23.8 ppm. Cross polarization under the Hartmann-Hahn match was obtained using 90° pulses of 5.0 μ s. The recycle time was 60 s. The number of transients varied from 4 to 128.

In all MAS NMR experiments, the magic angle was set by observing the FID arising from the ⁷⁹Br NMR of solid KBr (101). The accuracy was estimated to be within 0.5° .

Numerical calculations of the MAS NMR spectra were performed with FORTRAN-77 programs which incorporate the POWDER routine of Alderman, Solum and Grant (102) for powder averaging. Summations of spinning sidebands in ordinary MAS NMR spectra were performed using the program NMR-286 (Version 3, Release 2, 1991; T. Allman, SoftPulse Software, Guelph, Ontario, Canada).

4.8 Conclusions

In this chapter, MAS NMR spectra of homonuclear spin pairs have been investigated extensively from various special cases to general second-order spin pairs. Based on average Hamiltonian theory, a uniform treatment is developed in interpreting new observations concerning the spinning-frequency dependent behaviour of MAS NMR spectra. For the first time, high-order correction terms in the Magnus expansion series have been shown to have profound influences on MAS NMR spectra. The inclusion of high-order correction terms in the effective Hamiltonian also gives the possibility of interpreting some anomalous features that were previously observed in MAS NMR spectra but could not be understood with the first-order correction term alone. The results outlined in this chapter indicate that MAS NMR spectra arising from a simple two-spin system may exhibit complex behaviours in the slow spinning regime. It is important to be aware of these complex features in MAS NMR spectra so that one can draw correct conclusions concerning crystallographic equivalence and extract reliable NMR parameters from MAS NMR spectra.

Chapter 5

Variable-Angle-Spinning NMR Spectra of Homonuclear Two-Spin Systems

5.1 Introduction

As has been shown in Chapter 4, by rapid sample rotation at the magic angle (54.74°) with respect to the external magnetic field, anisotropic nuclear spin interactions can be completely or partially averaged, resulting in NMR spectra consisting of narrow peaks. However, the high resolution by using MAS is achieved at the expense of valuable anisotropic information. For example, information concerning the anisotropy in the chemical shielding is lost in NMR experiments which employ rapid magic-angle sample spinning. Several techniques have been developed to retrieve anisotropic information from high-resolution NMR spectra of solids. The most popular technique has involved slow sample spinning about the magic angle (65, 104). The sample spinning is said to be *slow* in a sense that the sample spinning frequency is smaller than the span of the static NMR spectrum (in frequency units). Under slow MAS conditions, spinning sidebands are observed at multiples of the spinning frequency. In principle, analysis of the relative intensities of the spinning sidebands allows one to reconstruct the static powder pattern and recover the anisotropic content of the spectrum (65, 104). However, this method is limited only to cases where the spin system consists of "isolated" spin- $\frac{1}{2}$ nuclei. A second and less frequently employed technique involves spinning the sample about an axis slightly off the magic angle (often denoted variable-angle-spinning, VAS)

(129,159,163-179). Lippmaa et al. (163) and Stejskal et al. (164) demonstrated that when a sample is spun at angles slightly off the magic angle, chemical shielding anisotropies can be reintroduced into NMR spectra as scaled powder patterns.

Although most of the previous VAS NMR studies were focused on retrieving chemical shielding anisotropies for ¹³C nuclei, several recent studies have appeared dealing with systems comprised of isolated spin pairs (129,159,172-177). For example, Grant and co-workers (174-176) investigated VAS NMR spectra of heteronuclear spin-pairs involving ¹³C and ¹⁴N nuclei. Nakai and McDowell (129,159) proposed the off-magic-angle-spinning technique for studying homonuclear dipolar-coupled spin pairs. One problem associated with VAS NMR studies of these dipolar-coupled spin pairs is that both the chemical shielding and dipolar interactions are scaled equally by rapid sample spinning about an axis off the magic angle. In principle, identical information will be available from NMR spectra of static samples (36,37,180). Obviously, it would be desirable if one could selectively scale only a single interaction in a VAS experiment.

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The focus of this chapter is homonuclear two-spin systems that consist of two crystallographically equivalent but magnetically non-equivalent spins. When a solid sample containing such a two-spin system is spun rapidly at the magic angle with respect to the external magnetic field, the MAS NMR spectrum consists of a single peak analogous to the situation in solution state NMR studies, that is, the *J* coupling between two crystallographically equivalent spins is not directly observable. However, as has been shown in Chapter 4, *J* coupling between two crystallographically equivalent spins can be determined by analyzing *slow* MAS NMR spectra. It is important to emphasize

that the reintroduction of J into MAS spectra requires two conditions to be satisfied. First, the two crystallographically equivalent spins must be coupled to one another *via* the direct dipole-dipole interaction. Second, the slow spinning condition must be met. Unfortunately, for a given spin system, the experimentalist has no control over the dipolar interaction, hence, it is not always possible to extract J from slow MAS NMR spectra. Moreover, under slow MAS conditions, NMR spectra are often complicated by spinning sidebands which arise from anisotropic chemical shielding and homonuclear dipolar interactions.

The objective of the study outlined in this chapter is to introduce new methods for J recoupling under more relaxed conditions. In §5.2, general theoretical expressions to describe NMR spectra under VAS conditions will be given. It will be shown in §5.3 that recoupling of J interactions occurs in VAS NMR spectra for any two-spin systems regardless of the magnitudes of the dipolar coupling. A two-dimensional (2D) VAS NMR technique for directly measuring J between two crystallographically equivalent spins will be described in §5.4. A brief summary will be given in §5.5.

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5.2 Theory

Under the *fast* VAS condition, *i.e.*, when the sample spinning frequency is much greater than the anisotropic interactions, the spin system can be described by a time-independent average Hamiltonian (18):

$$\mathcal{H}^{(0)} = \sum_{\lambda} \{ A_{00} T_{00}^{(\lambda)} + \frac{1}{2} (3 \cos^2 \theta_s - 1) A_{20} T_{20}^{(\lambda)} \}$$
(5.1)

where θ_S is the angle between the spinning axis and the external magnetic field; the various nuclear spin interactions λ are expressed in terms of spherical tensor operator A_{kq} and T_{kq} . Clearly, for spin systems consisting of spin-1/2 nuclei, the effect of rotating the sample at angles other than the magic angle ($\theta_S = 54.74^\circ$) is to introduce a scaling factor $\frac{1}{2}(3\cos^2\theta_S - 1)$ for chemical shift anisotropy and dipolar interactions whereas the isotropic J coupling constant remains intact. Consider a homonuclear two-spin system. The spin Hamiltonian for a particular crystallite under fast VAS conditions is given by Eq.(5.2) (18).

$$\mathcal{H}^{(0)} = -\omega_1' I_{1z} - \omega_2' I_{2z} + \omega_J I_1 \cdot I_2 + \omega_D' (3I_{1z}I_{2z} - I_1 \cdot I_2)$$
(5.2)

where

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$$\omega_{i}' = \omega_{iso}^{i} + \frac{\omega_{0}}{2} (3 \cos^{2} \theta_{s} - 1) (\sigma_{11}^{i} \sin^{2} \beta_{i}^{R} \cos^{2} \alpha_{i}^{R} + \sigma_{22}^{i} \sin^{2} \beta_{i}^{R} \sin^{2} \alpha_{i}^{R} + \sigma_{33}^{i} \cos^{2} \beta_{i}^{R})$$
(5.3)

$$\omega_{D}' = \frac{\pi R_{eff}}{2} (3 \cos^2 \theta_S - 1) (1 - 3 \cos^2 \theta_R)$$
 (5.4)

The angles α_i^R and β_i^R (i = 1 and 2) define the orientation of the sample spinning axis

in the principal-axis-system of the chemical shielding tensors for spins 1 and 2, respectively; see Fig.5.1. The angle θ_R is the angle between the dipolar vector and the sample spinning axis.

Note that the Hamiltonian in Eq.(5.2) is identical to that used for a static powder sample, except for the scaling factors in ω_i' and ω_D' (see Eq.(3.2)). Therefore, the frequencies and intensities of the NMR lines can be obtained:

$$\omega_1 = \frac{1}{2} (\omega_{\Sigma}' + \omega_J + 2\omega_D' + D), \qquad P_1 = 1 - \frac{\omega_J - \omega_D'}{D}; \qquad (5.5)$$

$$\omega_2 = \frac{1}{2} (\omega_{\Sigma}' - \omega_J - 2\omega_D' + D), \qquad P_2 = 1 + \frac{\omega_J - \omega_D'}{D}; \qquad (5.6)$$

$$\omega_{3} = \frac{1}{2} (\omega_{\Sigma}' + \omega_{J} + 2\omega_{D}' + D), \qquad P_{3} = 1 + \frac{\omega_{J} - \omega_{D}'}{D}; \qquad (5.7)$$

$$\omega_{4} = \frac{1}{2} (\omega_{\Sigma}' - \omega_{J} - 2\omega_{D}' - D), \qquad P_{4} = 1 - \frac{\omega_{J} - \omega_{D}'}{D}; \qquad (5.8)$$

where $\omega_{\Sigma}' = \omega_{I}' + \omega_{2}', \ \omega_{\Delta}' = \omega_{I}' - \omega_{2}'$ and

$$D = \left[\omega_{\Delta}'^{2} + \left(\omega_{J} - \omega_{D}' \right)^{2} \right]^{1/2}$$
(5.9)

The above equations indicate that, for a particular crystallite, the VAS NMR spectrum will exhibit a four-line spectrum that is similar to the "AB" spectrum for a single crystal. Since ω_{Δ}' and ω_{D}' in Eqs.(5.5)-(5.9) are orientation dependent, the second-order character present in the VAS NMR spectra will vary as a function of individual crystallite orientations with respect to the external magnetic field. More explicitly, the following three conditions may exist: (i) $|\omega_{\Delta}'| \ge |\omega_J - \omega_D'|$, (ii) $|\omega_{\Delta}'| \sim |\omega_J - \omega_D'|$
and (iii) $|\omega_{\Delta}'| \ll |\omega_J - \omega_D'|$. As has been demonstrated in Chapter 3, each of these conditions will generate distinct spectral features which are characteristic of first-order (AX), second-order (AB) and equivalent (A₂) spin systems, respectively. For a powdered sample, ω_{Δ}' and ω_D' vary depending on the crystallite orientation, therefore, the resultant VAS NMR spectrum will be a "mixture" or sum of a large number of AX, AB and A₂ spectra similar to the cases seen in Chapter 3.



Figure 5.1 Coordinate system used to define the orientation of the spinning axis in the principal-axis-system of the chemical shielding tensor.

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5.3 VAS NMR spectra of homonuclear spin-pairs consisting of two crystallographically equivalent spins

In this section, attention will be paid to a special case where the two crystallographically equivalent spins in the spin pair are only *J*-coupled to one another, *i.e.*, the direct dipole-dipole interaction between the two spins is negligible. This assumption is reasonable when the spinning angle is slightly off the magic angle. In other words, the scaling factor is close to zero, hence, the scaled dipolar interaction is usually much smaller than the J coupling.

5.3.1 Fast VAS NMR spectra for two J-coupled spins

If the direct dipole-dipole interaction between two crystallographically equivalent spins can be neglected in the VAS NMR experiments, the NMR resonances given in Eqs.(5.5)-(5.9) can be further simplified into:

$$\omega_1 = \frac{1}{2} (\omega_{\Sigma}' + \omega_J + D), \qquad P_1 = 1 - \frac{\omega_J}{D}; \qquad (5.10)$$

$$\omega_2 = \frac{1}{2} (\omega_{\Sigma}' - \omega_J + D), \qquad P_2 = 1 + \frac{\omega_J}{D}; \qquad (5.11)$$

$$\omega_3 = \frac{1}{2} (\omega_{\Sigma}' + \omega_J - D), \quad P_3 = 1 + \frac{\omega_J}{D};$$
 (5.12)

$$\omega_4 = \frac{1}{2} (\omega_{\Sigma}' - \omega_J - D), \quad P_4 = 1 - \frac{\omega_J}{D};$$
 (5.13)

where

$$D = \left[\omega_{\Delta}'^{2} + \omega_{J}^{2} \right]^{1/2}$$
 (5.14)

$$\omega_{\Sigma}' = \frac{\omega_{0}}{2} (3\cos^{2}\theta_{S} - 1) [\sigma_{11}(\sin^{2}\beta_{1}^{R}\cos^{2}\alpha_{1}^{R} + \sin^{2}\beta_{2}^{R}\cos^{2}\alpha_{2}^{R})$$

$$+ \sigma_{22}(\sin^{2}\beta_{1}^{R}\sin^{2}\alpha_{1}^{R} + \sin^{2}\beta_{2}^{R}\sin^{2}\alpha_{2}^{R}) + \sigma_{33}(\cos^{2}\beta_{1}^{R} + \cos^{2}\beta_{2}^{R})]$$

$$\omega_{\Delta}' = \frac{\omega_{0}}{2} (3\cos^{2}\theta_{S} - 1) [\sigma_{11}(\sin^{2}\beta_{1}^{R}\cos^{2}\alpha_{1}^{R} - \sin^{2}\beta_{2}^{R}\cos^{2}\alpha_{2}^{R}) + \sigma_{32}(\cos^{2}\beta_{1}^{R} - \cos^{2}\beta_{2}^{R})]$$

$$+ \sigma_{22}(\sin^{2}\beta_{1}^{R}\sin^{2}\alpha_{1}^{R} - \sin^{2}\beta_{2}^{R}\sin^{2}\alpha_{2}^{R}) + \sigma_{33}(\cos^{2}\beta_{1}^{R} - \cos^{2}\beta_{2}^{R})]$$
(5.16)

All possible values of α^R and β^R must be considered for a powder sample leading to powder lineshapes. In the absence of the *J* interaction, the VAS NMR spectrum will be a scaled lineshape solely due to anisotropic chemical shielding. To illustrate this scaling effect, several VAS ³¹P NMR spectra for solid tricyclohexylphosphine are shown in Fig.5.2. Clearly, the scaled powder lineshapes are reversed when the spinning angle passes through the magic angle. From the observed scaling factor, the spinning angle can be accurately determined. In the presence of the *J* coupling, however, the VAS powder lineshape will generally consist of four subspectra due to the four transitions described by Eqs.(5.10)-(5.13). More importantly, all four subspectra arising from a particular crystallite will be sensitive to the chemical shielding difference between the two spins, which in turn is determined by the relative orientation of the two chemical shielding tensors.

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Figure 5.2 Fast ³¹P VAS NMR spectra of solid tricyclohexylphosphine at 4.70 T.

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In Fig.5.3 theoretical VAS NMR spectra for two crystallographically equivalent J-coupled spins are shown as a function of the angle between B_0 and the sample spinning axis. Spinning at the magic angle, $\theta_s = 54.74^\circ$, leads to a single sharp isotropic peak. However, spinning at angles other than the magic angle results in broadened lineshapes which exhibit some fine structure. In particular, for smaller angles ($\theta_s = 50.00^\circ$ and $\theta_s = 52.00^\circ$ in Fig.5.3), the splittings between the break points at the high-frequency end of the VAS NMR spectra equal the J coupling constant. For angles only slightly off the magic angle (for example $\theta_s = 56.00^\circ$ in Fig.5.3), a triplet-like spectrum results; the separation between the mass centres of the outer weak peaks equals approximately 2J. Such spectra are analogous to tightly coupled AB spectra observed in solution NMR studies. For angles greater than the magic angle, the VAS NMR spectra show lineshapes similar to those obtained at angles less than the magic angle, except that the frequency scale is reversed (see Fig.5.3). This reversal arises because the scaling factor, $(3 \cos^2)$ θ_s - 1)/2, changes sign at the magic angle. Interestingly, the sensitivity of the VAS NMR spectra to variations in θ_s is more attenuated for angles greater than the magic angle, which is also a consequence of the orientation dependence of the scaling factor. Although VAS NMR spectra exhibit significantly different lineshapes depending on the sample spinning angle, the J coupling constant can always be readily obtained directly from the lineshapes. If θ_s deviates significantly from the magic angle, many distinct features can be resolved but it becomes increasingly difficult to extract a relatively small homonuclear spin-spin coupling constant from such spectra, *i.e.*, the relative resolution in VAS NMR spectra decreases.



Figure 5.3 Theoretical fast VAS NMR spectra arising from a pair of J-coupled crystallographically equivalent spins. Parameters used in the calculations are: $\nu_0\sigma_{11} = 6.0$, $\nu_0\sigma_{22} = -2.0$, $\nu_0\sigma_{33} = -4.0$ kHz and J = 250 Hz. The relative orientation of the two tensors is such that the two intermediate components, σ_{22} , are coincident and the least shielded component of spin 1, σ_{11} , is parallel to σ_{33} of spin 2. The two chemical shielding tensors are related by a C_2 axis.

As well as depending on the homonuclear J coupling, VAS NMR spectra also depend on the chemical shielding tensors of the two coupled crystallographically To illustrate the sensitivity of VAS NMR spectra to the relative equivalent spins. orientations of two symmetry related chemical shielding tensors involving J-coupled nuclei, three cases are considered in Fig.5.4. In each of the three cases, the two chemical shielding tensors are related by a C_2 axis. As seen in Fig.5.4, VAS NMR spectra change dramatically as the relative orientation of the two chemical shielding tensors is varied. Whenever two principal components of the two chemical shielding tensors become coincident, less AB character will be observed at frequencies corresponding to those orientations. This is most apparent in the spectrum shown at the top of Fig.5.4. When the σ_{11} components of the two shielding tensors are coincident, there is no splitting observable at the σ_{II} end of the VAS NMR spectrum. Note that the σ_{11} end of the spectrum corresponds to the high frequency (the left) end of the spectrum. At this orientation, the two spins actually constitute an A_2 spin system. As we have noted previously, the VAS NMR spectrum of a powdered sample is really a sum of many AX, AB and A₂ spectra. The spectrum shown at the bottom of Fig.5.4 illustrates this fact. First, the chemical shift difference at the σ_{II} directions is much greater than J, leading to AX spectral features. That is, the separation between the break points equals J. Second, since the σ_{22} principal components are coincident, a singlet-like feature predominates the σ_{22} region, which is typical of A₂ spectra. Finally, for the remaining orientations, complicated features are present, which are due to second order (AB) effects.



Figure 5.4 Theoretical fast VAS NMR spectra arising from two crystallographically equivalent spins with different relative orientations of the two chemical shielding tensors. $\theta_S = 50.00^\circ$, $\nu_0 \sigma_{11} = 6.0$, $\nu_0 \sigma_{22} = -2.0$, $\nu_0 \sigma_{33} = -4.0$ kHz and $\omega_J/2\pi = 250$ Hz. The relative orientations of the two chemical shielding tensors are also displayed. In each case the chemical shielding tensors are related by a C_2 axis.

5.3.2 Results and discussion

Experimental ³¹P VAS NMR spectra of Hg(PPh₃)₂(NO₃)₂ are displayed in Fig.5.5. Previous studies by X-ray crystallography (157) and fast MAS NMR (§4.4.2) indicate that the two ³¹P nuclei in Hg(PPh₃)₂(NO₃)₂, 15, are crystallographically equivalent but magnetically non-equivalent. In particular, the two phosphine ligands in $Hg(PPh_3)_2(NO_3)_2$ are related by a C_2 axis which bisects the P-Hg-P angle. When the sample spinning axis is at the magic angle with respect to the external field, the ${}^{31}P$ NMR spectrum exhibits a single isotropic peak with a linewidth of less than 30 Hz (see Fig.5.5). This confirms the crystallographic equivalence of the two³¹P nuclei. Spinning about angles other than the magic angle leads to VAS NMR spectra which exhibit some fine structure. Also, the breadth of the VAS NMR spectra increases dramatically as the sample spinning axis is tilted away from the magic angle. At angles slightly off the magic angle (for example $\theta_s = 51.00^\circ$ in Fig.5.5), a triplet-like spectrum results which, as already mentioned, resembles solution state NMR spectra arising from a very tightly J-coupled two-spin system. The separation between the weak outer peaks yields an estimate of 2J. A more accurate value for J, 250 ± 10 Hz, can be obtained directly from the NMR spectra acquired with the spinning axis further off-set from the magic angle; e.g., $\theta_s = 48.44^\circ$, see Fig.5.5. This value of the two-bond indirect phosphorusphosphorus coupling constant confirms the previous determinations of ${}^{2}J({}^{31}P,{}^{31}P)$ from J-recoupled slow MAS spectra and two-dimensional J-resolved spectra (§4.4.2).



Figure 5.5 Experimental and calculated fast VAS ³¹P NMR spectra of Hg(PPh₃)₂(NO₃)₂ at different sample rotation angles. The sample spinning rate is 4 kHz. Parameters used in the calculations are: $\nu_0 \sigma_{11} = 2.51$, $\nu_0 \sigma_{22} = -0.49$, $\nu_0 \sigma_{33} = -2.02$ kHz and $\omega_J/2\pi = 250$ Hz. The relative orientation of the two ³¹P chemical shielding tensors is given in the text and in Fig.5.6.

The calculated VAS ³¹P NMR spectra of Hg(PPh₃)₂(NO₃)₃ are also shown in Fig.5.5. In order to calculate these spectra, it was necessary to obtain the three principal components of the phosphorus chemical shielding tensor. Analysis of the static ³¹P NMR lineshape yielded the following values: $\sigma_{11} = 31$, $\sigma_{22} = -6$, and $\sigma_{33} = -25$ ppm. Note that these values are relative to the isotropic position. At the magnetic field strength used here, $B_0 = 4.70$ T, the span of the phosphorus chemical shielding tensor corresponds to 4.5 kHz. The sample spinning frequencies employed in this study, ≈ 4.0 kHz, were sufficient to satisfy the fast spinning condition. In fact, the intensities of all spinning sidebands in our VAS NMR spectra were negligible. The angles, θ_s , were measured directly as stated later in §5.5. Based on a ³¹P-³¹P separation of 4.474 Å which was determined for $Hg(PPh_3)_2(NO_3)_2$ by X-ray crystallography (157), the direct dipole-dipole coupling constant between the two ³¹P nuclei is only 220 Hz. In most of the VAS NMR experiments, the scaling factor was generally much less than 0.3. This leads to scaled ${}^{31}P{}^{-31}P$ dipolar couplings which have a negligible influence on the ${}^{31}P$ NMR lineshape. Also, the good agreement between the experimental and calculated VAS NMR spectra provides further evidence that the ³¹P-³¹P direct dipolar interaction can be safely ignored in the present system. That is, Eqs. (5.10)-(5.13) adequately describe the VAS NMR spectra of the ³¹P spin pair in Hg(PPh₃)₂(NO₃)₂.

Defining a coordinate system where the crystallographic C_2 axis is along the z direction, analyses of the ³¹P VAS NMR spectra of Hg(PPh₃)₂(NO₃)₂ yield the following ³¹P chemical shielding tensors (in ppm) with respect to the isotropic position:

$$\sigma^{(1)} = \begin{pmatrix} -4 & -2 & -21 \\ -2 & -4 & 18 \\ -21 & 18 & 8 \end{pmatrix} \text{ and } \sigma^{(2)} = \begin{pmatrix} -4 & -2 & 21 \\ -2 & -4 & -18 \\ 21 & -18 & 8 \end{pmatrix}$$

The orientations of the principal axes of the chemical shielding tensors are depicted in Fig.5.6. The σ_{11} component of each chemical shielding tensor makes an angle of 40° with respect to the C_2 axis.

In Fig.5.7 the ³¹P VAS NMR spectrum of Hg(PPh₃)₂(NO₃)₂ obtained at an angle significantly smaller than the magic angle ($\theta_S = 45.6^\circ$) is compared with the calculated spectrum. As anticipated, at this large offset, -9.1°, the total breadth of the VAS NMR lineshape increases and several fine features emerge. Again, the *J* coupling constant of 250 Hz is confirmed by the splittings between the outer break points as indicated in Fig.5.7. Using the same principal components and the relative orientations already mentioned, the main features of the observed spectrum can be reproduced by the theoretical lineshape calculations.

It is interesting to note that the Hamiltonian in Eq.(5.1) is identical to that used for a static sample (37), except for the scaling factor, $(3 \cos^2 \theta_s - 1)/2$. This indicates that some AB features must also exist in the static NMR spectrum. However, for a static sample there are very few orientations at which the chemical shift difference between the two spins is comparable to or smaller than J; so their contributions to the total NMR spectrum are generally negligible. In fact, second-order (AB) features purely due to a J coupling have not been observed in static NMR spectra of any system, although such features are frequently observed in MAS NMR spectra of isolated homonuclear spin



Figure 5.6 The orientations of the phosphorus chemical shielding tensors in $Hg(PPh_3)_2(NO_3)_2$. Note that only $\sigma^{(1)}$ is shown; $\sigma^{(2)}$ can be obtained by a 180° rotation about the C_2 axis.



Figure 5.7 Experimental (a) and calculated (b) 31 P fast VAS NMR spectrum of Hg(PPh₃)₂(NO₃)₂ obtained at $\theta_s = 45.6^{\circ}$. The sample spinning frequency is 4.0 kHz. Other parameters used in the calculation are identical to those used for calculating the VAS NMR spectra shown in Fig.5.5.

pairs as demonstrated in §4.6. In contrast to static NMR spectra, VAS scales the chemical shift difference to a considerable extent; this increases the number of orientations in which the chemical shift difference is comparable to or smaller than J, leading to a significant enhancement of AB features.

In many respects, the second-order (AB) features in VAS NMR spectra of *J*coupled spin pairs are similar to those in the static NMR spectra arising from two dipolar-coupled spins as discussed in §3.5. This is readily understood considering the similarity between the nuclear spin Hamiltonians that describe the two interactions. Of course, AB features in dipolar-coupled spin systems will be more complicated than those in VAS NMR spectra of *J*-coupled spin pairs, since the former interaction is also orientation dependent. Recently, Nakai and McDowell (*129,159*) considered theoretically the possibility of using the off-MAS technique to study dipolar-coupled spin pairs. As noted previously, there is no real improvement in relative spectral resolution compared with static NMR spectra. In contrast, the *J* interaction is independent of sample spinning; only the chemical shielding interaction is scaled by VAS. It is this fact which makes VAS NMR spectroscopy a superior technique for studying systems containing *J*coupled spin pairs.

Compared with dipolar-chemical shift NMR spectroscopy in static solids, one apparent disadvantage of using the VAS NMR method to study the relative orientations of chemical shielding tensors involving *J*-coupled spin pairs is the "scalar" property of the *J* interaction. This fact makes it impossible to relate chemical shielding tensors directly to the molecular frame. This certainly will be the case for general two-spin systems. Fortunately, for two crystallographically equivalent spins, the two chemical shielding tensors are always related by crystallographic symmetry elements such as C_2 axes; such a symmetry element can be used to relate the two chemical shielding tensors directly to the molecular frame.

In summary, it has been demonstrated that J coupling between two crystallographically equivalent but magnetically non-equivalent spins can be reintroduced into "high-resolution" solid-state NMR spectra by using the VAS technique. In contrast to previously reported J-recoupling phenomena observed under the slow MAS condition, the recoupling of J interactions under rapid VAS conditions does not depend on the homonuclear dipolar interaction between the two spins. Therefore, this type of Jrecoupling phenomenon is more general and will be observed for any crystallographically equivalent J-coupled spin pair.

In addition to the reintroduction of *J* coupling, the VAS NMR spectra are also sensitive to the mutual orientation of the chemical shielding tensors of two coupled spins. It has been shown that an analysis of VAS NMR lineshapes is capable of yielding such information. The advantages of this new method are: (i) VAS NMR spectra arising from two *J*-coupled spins can be analyzed in a straightforward way; (ii) second-order features are significantly enhanced in VAS NMR spectra whereas they are difficult or impossible to observe in static NMR spectra; (iii) VAS NMR spectra can be obtained at a number of different angles and from these independent spectra, more reliable results concerning the relative orientation of chemical shielding tensors can be extracted.

5.4 Direct determination of *J* coupling between two crystallographically equivalent spins by 2D VAS *J*-resolved experiments

As has been shown in §5.3, J coupling constant between two crystallographically equivalent spins can be extracted from VAS NMR spectra. In general, because VAS NMR lineshapes contain information concerning the J coupling as well as the dipolar and chemical shift interactions of the two coupled spins, thereby making an analysis difficult especially when all three interactions are unknown. It is therefore desirable to have a direct independent measurement of the J coupling constant. In this section, it will be demonstrated that, under VAS conditions, the two-dimensional (2D) J-resolved experiment can be used to provide an accurate determination of J coupling constant between two crystallographically equivalent spins. The important advantage of the 2D technique is that the determination of J is *independent* of both the dipolar interaction of the two spins and the relative orientation of the chemical shift tensors.

5.4.1 2D VAS J-resolved spectra

Since it is usually true that the dipolar coupling constant is much smaller than the chemical shift anisotropy, the scaled dipolar coupling in VAS experiments is usually much smaller than the scaled chemical shift difference between the two spins. Under this condition, Eq.(5.2) can be simplified into:

$$\mathfrak{H}^{(0)} = -\omega_1' I_{1z} - \omega_2' I_{2z} + \omega_J I_1 \cdot I_2 + 2\omega_D' I_{1z} I_{2z}$$
(5.17)

Clearly, Eq.(5.17) is of the same form as that used to describe solution-state NMR

spectra of two-spin systems. The only difference is that for isotropic fluids the last term of Eq.(5.17) is zero. Analogous to theoretical expressions derived to describe 2D Jspectrum of AB systems in solution state NMR studies, it is straightforward to obtain peak positions and amplitudes of a 2D J-resolved spectrum under VAS conditions. The results are listed in Table 5.1. Since ω_{Σ}' , ω_{Δ}' and ω_D' are orientation dependent, the

peak	F ₂	F ₁	amplitudes ^a
1	$\frac{1}{2}(\omega_{\Sigma}' + D + \omega_{I} + \omega_{D}')$	$+\frac{1}{2}(\omega_I + \omega_D')$	cos ² 2ξ
2	$\frac{1}{2}(\omega_{\Sigma}' + D - \omega_{I} - \omega_{D}')$	$-\frac{1}{2}(\omega_{I}+\omega_{D}')$	$\cos^2 2\xi$
3	$\frac{1}{2}(\omega_{\rm E}' - D + \omega_{\rm I} + \omega_{\rm D}')$	$+\frac{1}{2}(\omega_{I}+\omega_{D}')$	$\cos^2 2\xi$
4	$\frac{1}{2}(\omega_{\Sigma}' - D - \omega_J - \omega_D')$	$-\frac{1}{2}(\omega_J + \omega_D')$	$\cos^2 2\xi$
5	¹ / ₂ ($\omega_{\Sigma}' + D + \omega_J + \omega_D'$)	$\frac{1}{2}(D + \omega_J + \omega_D')$	-(1-sin 2ξ) sin 2ξ
б	$\frac{1}{2}(\omega_{\Sigma}' - D - \omega_J - \omega_D')$	$-\frac{1}{2}(D + \omega_J + \omega_D')$	$-(1-\sin 2\xi) \sin 2\xi$
7	$\frac{1}{2}(\omega_{\Sigma}' + D - \omega_{I} - \omega_{D}')$	$\frac{1}{2}(D - \omega_I - \omega_D')$	(1+sin 2ξ) sin 2ξ
8	$1/2(\omega_{\Sigma'} - D + \omega_J + \omega_D')$	$-\frac{1}{2}(D + \omega_J + \omega_D')$	$(1+\sin 2\xi) \sin 2\xi$
a .			

Table 5.1 The peak positions and the amplitudes in the 2D VAS *J*-resolved spectrum for a pair of crystallographically equivalent spins.

^a tan $2\xi = \omega_J / \omega_{\Delta}^{\prime}$.

eight peaks in the 2D VAS *J*-resolved spectrum will have "shapes" in both the F_I and F_2 dimensions. However, since ω_D' represents a scaled Pake doublet, the F_I projections of the peaks at $\frac{1}{2}(\omega_J + \omega_D')$ and $-\frac{1}{2}(\omega_J + \omega_D')$ will be symmetric about $\frac{1}{2}\omega_J$ and $-\frac{1}{2}\omega_J$, respectively. Therefore, the separation between them equals the *J*-coupling constant. Obviously, the peaks 5-8 listed in Table 5.1 arise from strong coupling effects

which may complicate the 2D spectra (vide infra). As has been mentioned previously, the 1D VAS NMR spectrum for a powder sample is the sum of a large number of AX, AB and A₂ spectra. However, no matter how complicated a 1D VAS NMR spectrum may appear, ω_J can always be directly obtained from the F_I projection of a 2D J-resolved spectrum.

5.4.3 Results and discussion

One-dimensional (1D) VAS ³¹P NMR spectra of Hg(PPh₃)₂(NO₃)₂, 15, have been shown in §5.3; see Fig.5.5. Since only ³¹P nuclei attached to a magnetically inactive mercury nucleus are of interest, satellite peaks due to coupling with ¹⁹⁹Hg ($I = \frac{1}{2}$) are not shown. Obviously, when the sample spinning axis is at the magic angle, the ${}^{31}P$ NMR spectrum of Hg(PPh₃)₂(NO₃)₂ exhibits a sharp isotropic peak indicating that the two ³¹P nuclei are crystallographically equivalent, in agreement with the result from an X-ray diffraction study (159). Clearly, the J coupling between the two ^{31}P nuclei is unavailable from the fast MAS spectrum of $Hg(PPh_3)_2(NO_3)_2$. When the spinning axis is set off the magic angle, the NMR spectra broaden and exhibit some fine structure. As has been demonstrated in §5.3, an analysis of the VAS ³¹P NMR lineshapes of $Hg(PPh_3)_2(NO_3)_2$ is capable of yielding information concerning ${}^2J({}^{31}P, {}^{31}P)$ and the relative orientation of the chemical shift tensors of the two ³¹P nuclei. In more general cases, especially when the homonuclear dipolar interaction is large, VAS NMR spectra may be more complex and the apparent splittings in the 1D VAS spectra do not correspond to J.

To obtain a direct measurement of ²J(³¹P,³¹P) for Hg(PPh₃)₂(NO₃)₂, 2D ³¹P Jresolved experiments were performed. The 2D ³¹P NMR spectra of Hg(PPh₃)₂(NO₃)₂ obtained with $\theta_s = 48.4^{\circ}$ and 45.6° are shown in Fig.5.8, together with the corresponding 1D VAS spectra. Interestingly, two pairs of intense peaks are present in the 2D spectrum obtained with $\theta_s = 48.4^{\circ}$. Along the F_1 axis the separation between the two peaks in each pair is 299 \pm 10 and 250 \pm 10 Hz for the high (left) and low (right) frequency pairs, respectively. This raises the question as to which separation corresponds to J. When the sample is spun at angles slightly off the magic angle, ω_{Δ} is small. This makes the amplitudes for peaks due to strong coupling effects large and their separation along the F_1 axis is close to the J coupling; see Table 1. However, as the spinning angle is further offset from the magic angle, peaks due to strong coupling effects should change their positions along the F_1 dimension, whereas the peaks separated by J will not change their positions. Clearly, from the 2D spectrum with $\theta_s = 45.6^\circ$, the peaks in the high frequency (left) pair move further apart from one another giving a separation along the F_1 dimension of 344 \pm 10 Hz, whereas the peaks in the low frequency (right) pair remain unchanged. This proves that the separation of 250 ± 10 Hz is the indirect spin-spin coupling constant between the two crystallographically equivalent ³¹P nuclei. This confirms the previous measurement of ${}^{2}J({}^{31}P, {}^{31}P)$ in Hg(PPh₃)₂(NO₃)₂ determined from slow MAS NMR spectra (§4.4.2). It is also interesting to compare the peak positions in the 2D spectra with the lineshapes in the 1D spectra. From the relative orientation of the two ³¹P chemical shift tensors, it is known that, at the two extremes of the 1D spectrum, the spin system can be described



Figure 5.8 2D VAS ³¹P J-resolved spectra of Hg(PPh₃)₂(NO₃)₂ at 4.70 T. The spinning angle is (a) $\theta_s = 48.4^{\circ}$ and (b) $\theta_s = 45.6^{\circ}$.

approximately as an AX system, whereas it is close to an A_2 system near the centre of the spectrum. Therefore, the splittings at the outer edges of the 1D lineshapes approximately equal the J coupling constant (the scaled dipolar coupling is small in the present case). The central sections of the 1D spectra exhibit a strong peak, which is typical for an A_2 system. These features are also apparent in the 2D J-resolved spectra. Again, the peak separation at the low frequency (right) end of the spectra equals J whereas the central part is associated with peaks which arise from strong coupling effects. Since the high-frequency end has much lower intensities, the F_1 splittings at this end are not clear. Also, intense features appear at $F_1 = 0$ near the central part of the spectra. In order to reduce the intensities of peaks arising from strong coupling effects, it is desirable to perform 2D J-resolved experiments at spinning angles far from the magic angle; however, such experiments will suffer from low sensitivity. In practice, it is more useful to perform 2D J-resolved experiments at spinning angles slightly off the magic angle as demonstrated here.

In summary, 2D VAS J-resolved experiments have been shown to be useful in providing a direct measurement of J between crystallographically equivalent spins. It is interesting to compare the proposed method with the recently reported J-recoupling phenomenon in slow MAS NMR spectra. The successful measurement of J from slow MAS spectra requires that the two crystallographically equivalent nuclei be coupled by the dipolar interaction. In contrast, the measurement of J from 2D VAS J-resolved spectra does not depend on the dipolar interaction between the two spins thereby making the method more general. In principle, this method is applicable to any homonuclear

two-spin system regardless of the magnitudes of the dipolar interaction. In addition, it is desirable to obtain VAS NMR spectra, since important information concerning the relative orientation of the two chemical shift tensors can be easily extracted from such spectra.

5.5 Experimental

All ³¹P VAS NMR spectra were recorded on a Bruker MSL-200 ($B_0 = 4.70$ T) spectrometer operating at a ³¹P NMR frequency of 81.03 MHz. A normal Bruker MAS probe and a Doty VAS probe were used. A white crystalline sample of Hg(PPh₃)₂(NO₃)₂, 15, was packed into a zirconium oxide rotor (7 mm o.d.). Crosspolarization under the Hartmann-Hahn match condition and high-power proton decoupling were employed for the acquisition of all ³¹P VAS NMR spectra. Typical ¹H 90° pulses were 4.5-5.0 μ s and a contact time of 5 ms was used for all experiments. The angle between the applied magnetic field and the spinning axis was determined by measuring the scaling factor from VAS ³¹P NMR spectra of solid tricyclohexylphosphine (see Fig.5.2). In the experiments described in this chapter, this angle was confined to the range 40° to 60°. A standard pulse sequence (138) employing a 32 phase-cycling scheme was used to obtain solid-state ³¹P 2D VAS J-resolved spectra with CP. All 2D J-resolved spectra were obtained in the magnitude mode. A total of 64 t_1 increments were taken in the 2D experiments and the size of the 2D data set was 128 by 2 K. A recycle time of 30 s was used to acquire both the 1D and 2D spectra. The sample spinning frequencies were 3.5-4.0 kHz, sufficient to satisfy the fast spinning condition.

Numerical calculations of ³¹P VAS NMR spectra were based on Eqs.(5.10)-(5.13) and were performed with a FORTRAN program. The POWDER routine of Alderman, Solum, and Grant (*102*) was incorporated into the program for powder averaging.

5.6 Conclusions

In this chapter, two new applications of VAS NMR spectroscopy are described. For the first time, a J-recoupling phenomenon has been observed in VAS NMR spectra arising from a pair of crystallographically equivalent spins. It has been demonstrated that a direct determination of J coupling constant between two crystallographically equivalent spins can be obtained from 2D VAS J-resolved NMR spectra. The advantage of the 2D VAS J-resolved experiment in measuring J is that the method is independent of the relative orientation of the two chemical shift tensors and the dipolar interaction between the two coupled spins. The most important result in this chapter is the idea that information concerning the relative orientation of chemical shift tensors can be extracted from VAS NMR spectra. This new method of extracting orientation information of chemical shift tensors does not depend on the dipolar interaction between the two spins, in contrast to the well-known dipolar-chemical shift NMR method. In principle, this VAS NMR method is applicable to any homonuclear two-spin system and will have great advantages for J-coupled spin pairs where the usual dipolar-chemical shift method is not applicable.

Chapter 6

Concluding Remarks

NMR spectroscopy of solids has become a feasible technique widely used in the study of a great variety of solid materials. Traditionally, chemists have been interested only in NMR spectra consisting of narrow peaks, *i.e.*, "liquid-like" spectra. Although it is well-known that there is more information in solid-state NM^k spectra, the problem has been to devise techniques to extract the chemically useful information content from such spectra. This thesis has been concerned with the question of how the anisotropic nuclear spin interactions influence solid-state NMR spectra arising from homonuclear First, it was demonstrated that, for homonuclear spin-pair systems spin systems. consisting of magnetically dilute nuclei, information concerning the orientation of the chemical shift tensors can be extracted from NMR spectra of both static and rotating solids. Second, it was shown that anisotropic chemical shielding and dipolar interactions are responsible for the anomalous features observed in MAS NMR spectra of homonuclear spin pairs. Clearly, solid state NMR provides one with the opportunity to explore the anisotropic nature of nuclear spin interactions. In recent years, considerable attention has been paid to the three-dimensional nature of various nuclear spin interactions. For example, the number of experimental NMR studies reporting chemical shift tensors, instead of reporting isotropic chemical shifts alone, has started to grow in major chemistry journals. There is no doubt that information concerning the anisotropic nature of nuclear spin interactions will provide a more complete description of chemical reality.

The work outlined in this thesis can be extended possibly in the following three directions. First, since static NMR spectra contain information concerning both chemical shielding and dipolar interactions, it will be extremely useful if the dipolar coupling constant can be determined independently by other NMR methods. With the knowledge of the dipolar coupling constant, analysis of static NMR spectra can be simplified. Second, it was observed experimentally that spinning sidebands in MAS NMR spectra of homonuclear multi-spin systems often exhibit interesting features. The detailed spinning sideband structures cannot be accounted for using the theoretical methods outlined in this thesis. It will be of interest if the observed spinning sidebands can be reproduced with other methods such as the numerical method of Levitt et al. (125). This will lead to a new way of extracting information concerning the orientation of chemical shielding tensors. Third, it is clear that the VAS techniques outlined in this thesis are also applicable to general homonuclear two-spin systems. Also, since the fast spinning condition may not always be practical, it will be useful to study VAS NMR spectra under slow spinning conditions.

Appendix I

Basic product operators for two-spin (I=1/2) systems

Taking the products $|\alpha\alpha\rangle$, $|\alpha\beta\rangle$, $|\beta\alpha\rangle$ and $|\beta\beta\rangle$ as basic wave functions for a two-spin (I=1/2) system, the sixteen basic product operators have the following forms.

The unity matrix

ŧ

$$E = \left(\begin{array}{rrrrr} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{array}\right)$$

The population operators

$$2I_{1z}I_{2z} = \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$
$$I_{1z} = \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$
$$I_{2z} = \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

The single-quantum coherence operators

- I

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.

$$\begin{split} I_{1x} &= \frac{1}{2} \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix} \qquad I_{2x} &= \frac{1}{2} \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \\ I_{1y} &= \frac{1}{2} \begin{bmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & -i \\ i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{bmatrix} \qquad I_{2y} &= \frac{1}{2} \begin{bmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix} \qquad 2I_{1z}I_{2x} = \frac{1}{2} \begin{bmatrix} 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix} \qquad 2I_{1z}I_{2y} = \frac{1}{2} \begin{bmatrix} 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \\ 2I_{1y}I_{2z} &= \frac{1}{2} \begin{bmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & i \\ i & 0 & 0 & 0 \\ 0 & -i & 0 & 0 \end{bmatrix} \qquad 2I_{1z}I_{2y} = \frac{1}{2} \begin{bmatrix} 0 & -i & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & i \\ 0 & 0 & -i & 0 \end{bmatrix} \end{split}$$

The zero- and double-quantum coherence operators

$$2I_{1x}I_{2y} = \frac{1}{2} \begin{pmatrix} 0 & 0 & 0 & i \\ 0 & 0 & -i & 0 \\ 0 & i & 0 & 0 \\ -i & 0 & 0 & 0 \end{pmatrix} \qquad 2I_{1y}I_{2x} = \frac{1}{2} \begin{pmatrix} 0 & 0 & 0 & i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ -i & 0 & 0 & 0 \end{pmatrix}$$

$$2I_{1x}I_{2x} - \frac{1}{2} \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} \qquad 2I_{1y}I_{2y} - \frac{1}{2} \begin{bmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{bmatrix}$$

It is sometimes useful to use the raising and lowering operators, I_+ and I_- .

Therefore, the so-called "flip-flop" term has the following form:

$$I_{1+}I_{2-} + I_{1-}I_{2+} = \left(\begin{array}{cccc} 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{array}\right)$$

IJ

Appendix II

Analysis of NMR spectra arising from an isolated two-spin

system in static solids

Consider two like spins 1 and 2 which are coupled by the dipolar and J interactions and have anisotropic chemical shifts. The approprite Hamiltonian is:

$$\mathcal{H} - \omega_1 I_{1z} - \omega_2 I_{2z} + \omega_J I_1 \cdot I_2 + \omega_D (3I_{1z}I_{2z} - I_1 \cdot I_2)$$
(A2.1)

Using the basic product operators given in Appendix I, one can write the above Hamiltonian in the following matrix form:

$$\mathcal{H} = \frac{1}{2} \begin{bmatrix} -\omega_{1} - \omega_{2} + \frac{\omega_{J}}{2} + \omega_{D} & 0 & 0 & 0 \\ 0 & -\omega_{1} + \omega_{2} - \frac{\omega_{J}}{2} - \omega_{D} & \omega_{J} - \omega_{D} & 0 \\ 0 & \omega_{J} - \omega_{D} & \omega_{1} - \omega_{2} - \frac{\omega_{J}}{2} - \omega_{D} & 0 \\ 0 & 0 & 0 & \omega_{1} + \omega_{2} + \frac{\omega_{J}}{2} + \omega_{D} \end{bmatrix}$$
(A2.2)

Diagonalization of the above matrix gives the following eigenvalues (in units of \hbar) and eigenfunctions:

$$E_1 = -\frac{\omega_1}{2} - \frac{\omega_2}{2} + \frac{\omega_J}{4} + \frac{\omega_D}{2} ; \quad \psi_1 = |\alpha\alpha\rangle$$
(A2.3)

$$E_{2} - \frac{\omega_{J}}{4} - \frac{\omega_{D}}{2} - \frac{D}{2} \quad ; \psi_{2} - \frac{1}{(1+Q^{2})^{\frac{1}{2}}} \{ Q \mid \alpha\beta \rangle - |\beta\alpha\rangle \} \quad (A2.4)$$

$$E_{3} = -\frac{\omega_{J}}{4} - \frac{\omega_{D}}{2} + \frac{D}{2} \qquad ; \quad \psi_{3} = \frac{1}{(1+Q^{2})^{\frac{1}{2}}} \left\{ |\alpha\beta\rangle + Q |\beta\alpha\rangle \right\} (A2.5)$$

$$E_4 = \frac{\omega_1}{2} + \frac{\omega_2}{2} + \frac{\omega_J}{4} + \frac{\omega_D}{2} \quad ; \quad \psi_4 = |\beta\beta\rangle \tag{A2.6}$$

where

$$D = [(\omega_1 - \omega_2)^2 + (\omega_J - \omega_D)^2]^{\frac{1}{2}}$$
(A2.7)

$$Q = \frac{\omega_J - \omega_D}{D - (\omega_1 - \omega_2)}$$
(A2.8)

For this energy level system, there are four observable NMR transitions as indicated in Fig.A2.1.



Figure A2.1 The four observable NMR transitions in a two-spin system.

The transition probability for $\psi_i \rightarrow \psi_j$ is given by the following expression:

$$P \propto |\langle \psi_i | (I_{1-} + I_{2-}) | \psi_j \rangle|^2$$
(A2.9)

For example, the transition prabability for $\psi_1 \rightarrow \psi_2$ is given by

$$P \propto |\langle \psi_{1} | (I_{1-} + I_{2-}) | \psi_{2} \rangle|^{2}$$

$$= |\langle \alpha \alpha | (I_{1-} + I_{2-}) \frac{1}{(1 + Q^{2})^{1/2}} (Q | \alpha \beta \rangle - |\beta \alpha \rangle)|^{2}$$

$$= \frac{(Q - 1)^{2}}{1 + Q^{2}} = 1 - \frac{\omega_{J} - \omega_{D}}{D}$$
(A2.10)

Similarly, the transition probability for other transitions can also be calculated and the results are given below.

Transition	Frequency relative to $\frac{1}{2}(\omega_1 + \omega_2)$	Intensity
$\psi_1 \rightarrow \psi_2$	$-D/2 - (\omega_J + 2\omega_D)/2$	$1 - (\omega_J - \omega_D)/D$
$\psi_3 \rightarrow \psi_4$	$-D/2 + (\omega_J + 2\omega_D)/2$	$1 + (\omega_J - \omega_D)/D$
$\psi_l \rightarrow \psi_3$	$+D/2 - (\omega_J + 2\omega_D)/2$	$1 + (\omega_J - \omega_D)/D$
$\psi_2 \rightarrow \psi_4$	$+D/2 + (\omega_J + 2\omega_D)/2$	$1 - (\omega_J - \omega_D)/D$

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