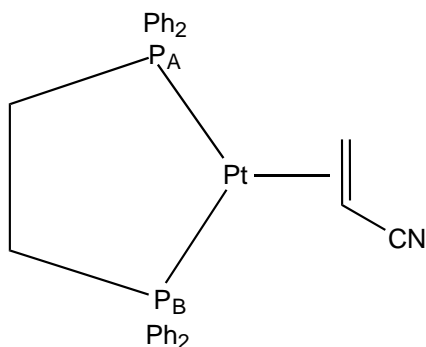


Introduction

This experiment involves the analysis of the nuclear magnetic resonance spectrum of the two ^{31}P nuclei, A and B, in the novel platinum compound shown below¹, $\text{Pt}(\text{dppe})(\text{CH}_2\text{CHCN})$, where $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$:



Analysis of this spectrum affords an excellent example of the use of the quantum theory of angular momentum in nuclear spin systems. In what follows, a thorough familiarity with the angular momentum topics discussed in lecture is assumed.

The appearance of the NMR spectrum of a molecule is determined by the chemical shifts and spin-spin coupling constants of the nuclei. These in turn depend in a complex way on the electronic structure of the molecule. However, a detailed description of such electronic effects will not concern us here, and they will be absorbed in the chemical shift and the spin-spin coupling parameters. In a system containing two phosphorus nuclei, there are two parameters involved: the relative chemical shift between the two phosphorus nuclei, symbolized δ (a dimensionless number expressing the shift in parts per million, ppm, of the nominal resonance frequency), and the spin-spin coupling constant, J (expressed as a frequency in Hz). The case to be treated in this lab is an example in which the energy hJ approaches the order of magnitude of the energy $h\nu_0\delta$, ($h\nu_0 = g_N\beta_N H$ with H the magnetic field strength), so that a full quantum-mechanical analysis is required in order to determine J and δ from the spectrum.

¹This molecule, which is an important intermediate in a synthetic scheme involved in one of the research projects in Professor Glueck's laboratory. It was first synthesized by Dr. Igor Kourkine, a recent Dartmouth PhD student with Prof. Glueck.

Theory

The starting point of the calculation is the nuclear spin Hamiltonian for two nuclei A and B:

$$\hat{H} = -\frac{g_N \beta_N}{\hbar} \mathbf{H} \cdot \left\{ (1 - \sigma_A) \hat{\mathbf{I}}_A + (1 - \sigma_B) \hat{\mathbf{I}}_B \right\} + \frac{hJ}{\hbar^2} \hat{\mathbf{I}}_A \cdot \hat{\mathbf{I}}_B$$

where

$\hat{\mathbf{I}}_A$ and $\hat{\mathbf{I}}_B$ are the spin angular momentum operators for the nuclei
 \mathbf{H} = applied magnetic field (vector quantities are in **bold** type)
 A,B are two chemically non-equivalent phosphorus nuclei
 σ_A , σ_B are the chemical shifts for nucleus A and B, respectively
 δ is the relative chemical shift, $\sigma_A - \sigma_B$.

Since a ^{31}P nucleus has a nuclear spin quantum number $I = 1/2$, a single phosphorus nucleus has two possible spin states—denoted α or β . Thus, the four simple product nuclear spin functions

$$\Psi_1 = \alpha_A \alpha_B ; \Psi_2 = \alpha_A \beta_B ; \Psi_3 = \beta_A \alpha_B ; \text{ and } \Psi_4 = \beta_A \beta_B$$

form a complete set of **orthonormal** functions for two $I = 1/2$ nuclear spins, and any two-spin function can be written as a linear combination of Ψ_1 , Ψ_2 , Ψ_3 , and Ψ_4 . Here, we take the general trial function

$$\phi = \mathbf{a}\Psi_1 + \mathbf{c}\Psi_2 + \mathbf{d}\Psi_3 + \mathbf{b}\Psi_4$$

where **a**, **b**, **c**, and **d** are, as yet, unknown coefficients. (Note the order in which they appear in ϕ !) Recall that we can determine the values of such coefficients by requiring that they minimize the variational expression for the energy²:

$$\langle E \rangle \equiv E_\phi = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle}.$$

That is, **a**, **b**, **c** and **d** are chosen so that the following conditions are met:

$$\frac{\partial E_\phi}{\partial \mathbf{a}} = 0 ; \frac{\partial E_\phi}{\partial \mathbf{b}} = 0 ; \frac{\partial E_\phi}{\partial \mathbf{c}} = 0 ; \frac{\partial E_\phi}{\partial \mathbf{d}} = 0.$$

²The shorthand notation $\langle \phi | \hat{H} | \phi \rangle$ and $\langle \phi | \phi \rangle$ stand for the usual integrals of variation theory.

These conditions give rise to the four secular equations given below.

$$\begin{aligned} (H_{11} - E) \mathbf{a} + H_{12} \mathbf{c} + H_{13} \mathbf{d} + H_{14} \mathbf{b} &= 0 \\ H_{21} \mathbf{a} + (H_{22} - E) \mathbf{c} + H_{23} \mathbf{d} + H_{24} \mathbf{b} &= 0 \\ H_{31} \mathbf{a} + H_{32} \mathbf{c} + (H_{33} - E) \mathbf{d} + H_{34} \mathbf{b} &= 0 \\ H_{41} \mathbf{a} + H_{42} \mathbf{c} + H_{43} \mathbf{d} + (H_{44} - E) \mathbf{b} &= 0 \end{aligned}$$

where, for example, $H_{32} = \langle \Psi_3 | \hat{H} | \Psi_2 \rangle$, and we have used the orthonormal properties of the Ψ 's to write $\langle \Psi_3 | \Psi_3 \rangle = 1$, $\langle \Psi_3 | \Psi_2 \rangle = 0$, etc. A set of equations such as these (which are called linear, homogeneous equations) will have a non-trivial solution (i.e., a solution other than $\mathbf{a} = \mathbf{b} = \mathbf{c} = \mathbf{d} = 0$) if and only if the so-called secular determinant is zero:

$$\begin{vmatrix} (H_{11} - E) & H_{12} & H_{13} & H_{14} \\ H_{21} & (H_{22} - E) & H_{23} & H_{24} \\ H_{31} & H_{32} & (H_{33} - E) & H_{34} \\ H_{41} & H_{42} & H_{43} & (H_{44} - E) \end{vmatrix} = 0.$$

Thus, the wavefunctions ϕ for this A–B two-spin system will have variational coefficients that are the solutions to the secular equations with energies given by the roots of the secular determinant polynomial in E . It is clear that we must evaluate H_{11} , H_{12} , etc., to complete these solutions. The rest of the theory section (essentially the whole section) is to be developed by each student independently following the steps outlined below.

Theoretical Calculations

Taking the applied magnetic field vector, \mathbf{H} , as defining the z direction we may as usual rewrite the spin Hamiltonian as:

$$\hat{H} = -\frac{h\nu_0}{\hbar} \{ (1 - \sigma_A) \hat{I}_{zA} + (1 - \sigma_B) \hat{I}_{zB} \} + \frac{hJ}{\hbar^2} \hat{\mathbf{I}}_A \cdot \hat{\mathbf{I}}_B$$

where $h\nu_0 \cong g_N \beta_N H$ has been introduced.³

Expand $\hat{\mathbf{I}}_A \cdot \hat{\mathbf{I}}_B$ in terms of $\hat{I}_{+(A)}$, $\hat{I}_{-(A)}$, $\hat{I}_{+(B)}$, $\hat{I}_{-(B)}$, $\hat{I}_{z(A)}$, and $\hat{I}_{z(B)}$, by first writing $\hat{\mathbf{I}}_A \cdot \hat{\mathbf{I}}_B$ in terms of Cartesian components $\hat{I}_{x(A)}$ etc., and then writing \hat{I}_x and \hat{I}_y in terms of \hat{I}_+ and

³This approximation, where ν_0 is the standard spectrometer frequency (121.426 MHz) is possible since any phosphorus spin comes into resonance within a few parts in 10^5 of all other phosphorus nuclei.

\hat{I}_- . You should obtain

$$\hat{\mathbf{I}}_A \cdot \hat{\mathbf{I}}_B = \frac{1}{2} (\hat{I}_{+(A)} \hat{I}_{-(B)} + \hat{I}_{-(A)} \hat{I}_{+(B)}) + \hat{I}_{z(A)} \hat{I}_{z(B)}.$$

Next, we will start to evaluate H_{11} , H_{23} , etc., in the following steps. Find the value of $\hat{H}\Psi_i$ for each of the product spin functions Ψ_1 , Ψ_2 , Ψ_3 , and Ψ_4 . You should find, for example,

$$\hat{H}\Psi_1 = \left\{ h\nu_0 \left(-1 + \frac{\sigma_A + \sigma_B}{2} \right) + \frac{hJ}{4} \right\} \Psi_1$$

$$\hat{H}\Psi_4 = \left\{ h\nu_0 \left(1 - \frac{\sigma_A + \sigma_B}{2} \right) + \frac{hJ}{4} \right\} \Psi_4.$$

This shows that

(i) Ψ_1 and Ψ_4 are eigenfunctions of \hat{H} with energies (eigenvalues) E_1 and E_4 :

$$E_1 = h\nu_0 \left(-1 + \frac{\sigma_A + \sigma_B}{2} \right) + \frac{hJ}{4}$$

$$E_4 = h\nu_0 \left(1 - \frac{\sigma_A + \sigma_B}{2} \right) + \frac{hJ}{4}$$

(ii) $\langle \Psi_1 | \hat{H} | \Psi_1 \rangle = E_1$, but $\langle \Psi_j | \hat{H} | \Psi_1 \rangle = 0$, $j \neq 1$
 $\langle \Psi_4 | \hat{H} | \Psi_4 \rangle = E_4$, but $\langle \Psi_j | \hat{H} | \Psi_4 \rangle = 0$, $j \neq 4$

Thus, the secular determinant becomes

$$\begin{vmatrix} (H_{11} - E) & 0 & 0 & 0 \\ 0 & (H_{22} - E) & H_{23} & 0 \\ 0 & H_{32} & (H_{33} - E) & 0 \\ 0 & 0 & 0 & (H_{44} - E) \end{vmatrix} = 0.$$

This 4×4 determinant factors into the two trivial equations

$$(H_{11} - E) = 0 \quad \text{and} \quad (H_{44} - E) = 0$$

and the 2×2 determinantal equation

$$\begin{vmatrix} (H_{22} - E) & H_{23} \\ H_{32} & (H_{33} - E) \end{vmatrix} = 0.$$

Substituting the root $E_1 = H_{11}$ back into the secular equations gives $\mathbf{a} = a$ constant (which we take to be 1 for normalization purposes) and $\mathbf{b} = \mathbf{c} = \mathbf{d} = 0$ for the first spin state, i.e., $\phi_1 = \Psi_1$.

Repeating the procedure with the root $E_4 = H_{44}$ gives similarly $\mathbf{a} = \mathbf{c} = \mathbf{d} = 0$ and $\mathbf{b} = 1$, i.e., $\phi_4 = \Psi_4$. This is consistent with our earlier statement that Ψ_1 and Ψ_4 are eigenfunctions of \hat{H} .

Next, simplify the expressions for $\hat{H}\Psi_2$ and $\hat{H}\Psi_3$. Notice that $\hat{H}\Psi_2$ contains both Ψ_2 and Ψ_3 and that $\hat{H}\Psi_3$ does, too. This is good evidence that linear combinations of Ψ_2 and Ψ_3 will be found to be eigenfunctions of \hat{H} . The next step is the evaluation of H_{22} , H_{23} , (which equals H_{32} , since \hat{H} is Hermitian and all the H matrix elements are purely real), and H_{33} . Once we have these, solving the 2×2 secular determinant will produce the remaining spin states as outlined below.

Expand the 2×2 secular determinant, and use the quadratic formula to write two expressions for E; denote one by E_+ and the other by E_- (for reasons that will be obvious). After a little simplification, the result should be

$$E_{\pm} = [(H_{33} + H_{22}) \pm D]/2$$

where

$$D = [(H_{33} - H_{22})^2 + 4H_{32}^2]^{1/2}.$$

The + sign goes with E_+ ; the - sign, with E_- . E_+ may be substituted into either secular equation on which the 2×2 secular determinant is based to establish a value for the ratio of the two coefficients, \mathbf{d}/\mathbf{c} . We will denote this ratio by $\mathbf{d}_+/\mathbf{c}_+$ for obvious reasons. You should note that substitution of E_+ back into the other secular equation must give a redundant expression for $\mathbf{d}_+/\mathbf{c}_+$, i.e., with $E = E_+$, the two secular equations are no longer independent. (To prove the equivalence of the two possible expressions for $\mathbf{d}_+/\mathbf{c}_+$, one can form the product $(\mathbf{c}_+/\mathbf{d}_+)_{(\text{from one equation})} \times (\mathbf{d}_+/\mathbf{c}_+)_{(\text{from the other equation})}$ and simplify to show that this product equals 1.)

In any case, if you use the secular equation $(H_{22} - E_+) \mathbf{c}_+ + H_{23} \mathbf{d}_+ = 0$, you should find that

$$\frac{\mathbf{d}_+}{\mathbf{c}_+} = \frac{H_{33} - H_{22} + D}{2H_{23}}$$

where D was defined above.

An additional equation relating \mathbf{c}_+ and \mathbf{d}_+ is obtained by requiring the eigenfunction to be normalized. Denoting the eigenfunction by ϕ_2 we have

$$\phi_2 = \mathbf{c}_+ \Psi_2 + \mathbf{d}_+ \Psi_3.$$

Prove that requiring ϕ_2 to be normalized, i.e., $\langle \phi_2 | \phi_2 \rangle = 1$, is equivalent to requiring that

$$\mathbf{c}_+^2 + \mathbf{d}_+^2 = 1.$$

This equation suggests a convenient substitution. We write $\mathbf{c}_+ = \cos \theta$ and $\mathbf{d}_+ = \sin \theta$. Reduction to a one variable problem (θ) from a two variable problem (\mathbf{c}_+ and \mathbf{d}_+) is justified because this substitution automatically guarantees normalization. With this substitution, the expression for $\mathbf{d}_+/\mathbf{c}_+$ is

$$\frac{\mathbf{d}_+}{\mathbf{c}_+} = \frac{\sin \theta}{\cos \theta} = \tan \theta = \frac{H_{33} - H_{22} + D}{2H_{23}}.$$

Thus once the integrals on the right hand side are evaluated, $\tan \theta$ and hence \mathbf{c}_+ and \mathbf{d}_+ are determined.

The coefficients of the wavefunction having eigenvalue E_- are found by substituting the expression for E_- into one of the secular equations. The algebra turns out to be simple if one uses the secular equation $H_{32} \mathbf{c}_- + (H_{33} - E_-) \mathbf{d}_- = 0$. You should find

$$\frac{\mathbf{c}_-}{\mathbf{d}_-} = \frac{-(H_{33} - H_{22} + D)}{2H_{32}}$$

which by inspection means (since $H_{32} = H_{23}$)

$$\frac{\mathbf{c}_-}{\mathbf{d}_-} = \frac{-\sin \theta}{\cos \theta} = -\tan \theta.$$

Since $\phi_3 = \mathbf{c}_- \Psi_2 + \mathbf{d}_- \Psi_3$ must be normalized, we choose $\mathbf{c}_- = -\sin \theta$ and $\mathbf{d}_- = \cos \theta$. (The signs could just as well be reversed since in general Ψ and $-\Psi$ have the same physical significance.)

In summary, you should have proved up to this point that:

$$\phi_1 = \Psi_1 \quad \text{with energy} = E_1$$

$$\phi_2 = \cos \theta \Psi_2 + \sin \theta \Psi_3 \quad \text{with energy} = E_+$$

$$\phi_3 = -\sin \theta \Psi_2 + \cos \theta \Psi_3 \quad \text{with energy} = E_-$$

$$\phi_4 = \Psi_4 \quad \text{with energy} = E_4$$

where θ is determined by

$$\tan \theta = \frac{H_{33} - H_{22} + D}{2H_{23}}.$$

It is now time to explore the right hand side of this equation in terms of the physical variables δ , J , and the NMR frequency, ν_0 . To do this, calculate values for all quantities which appear on the right-hand side; namely, the integrals H_{22} , H_{33} , and H_{23} . This is a very simple chore if you have already worked out $\hat{H}\Psi_2$ and $\hat{H}\Psi_3$. Your results should compare favorably with the following:

$$H_{22} = h\nu_0 \left(\frac{\sigma_A - \sigma_B}{2} \right) - \frac{hJ}{4} = \frac{h\nu_0 \delta}{2} - \frac{hJ}{4}$$

$$H_{23} = H_{32} = \frac{hJ}{2}$$

$$H_{33} = -h\nu_0 \left(\frac{\sigma_A - \sigma_B}{2} \right) - \frac{hJ}{4} = -\frac{h\nu_0 \delta}{2} - \frac{hJ}{4}.$$

With these values in hand, the equation for E_{\pm} can be rewritten:

$$E_{\pm} = \pm \left[\left(\frac{h\nu_0 \delta}{2} \right)^2 + \left(\frac{hJ}{2} \right)^2 \right]^{1/2} - \frac{hJ}{4} = \pm \frac{D}{2} - \frac{hJ}{4}.$$

Construct an energy level diagram for the four state system ϕ_1 , ϕ_2 , ϕ_3 , and ϕ_4 . Remember that hJ and $h\nu_0\delta$ are of the same order of magnitude and that δ is a very small number (parts per million). It will not be possible to make this diagram to scale, but at least indicate that $\delta \ll 1$. It will probably prove best to "build up" the energy level diagram in stages (one term at a time).

Now, of course, we must consider how many of the six potential absorptions are actually observable. We must calculate transition dipole selection rules for the various possibilities. We will do slightly more than calculate selection rules (which

only say “yes” or “no” to a particular transition)—we will calculate relative intensities.

It is sufficient to examine transitions resulting from the x component of the perturbation operator, $(\hat{V}_{nmr})_x = -(\mathbf{H}_1)_x (\hat{\mu}_N)_x$ where $(\hat{\mu}_N)_x = g_N \beta_N \hat{I}_{x(T)}$, the magnetic dipole moment x component for the nuclear spin system. Thus, considering only the major factors that control the magnitude of the transition moment vector, \mathbf{R} , for different transitions from initial state Ψ_i to final state Ψ_f , we can write the proportionalities

$$(\mathbf{R}_{if})_x \propto -g_N \beta_N (\mathbf{H}_1)_x \langle \Psi_f | \hat{I}_{x(T)} | \Psi_i \rangle \propto \langle \Psi_f | \hat{I}_{x(T)} | \Psi_i \rangle.$$

But

$$\hat{I}_{x(T)} = \hat{I}_{x(A)} + \hat{I}_{x(B)}$$

and the right hand side can be written in terms of the operators \hat{I}_+ and \hat{I}_- as

$$\hat{I}_{x(T)} = \frac{\hat{I}_{+(A)} + \hat{I}_{+(B)} + \hat{I}_{-(A)} + \hat{I}_{-(B)}}{2}.$$

Dropping the 2 in the denominator, we finally arrive at the important proportionality

$$(\mathbf{R}_{if})_x \propto \langle \Psi_f | \hat{I}_{+(A)} + \hat{I}_{+(B)} + \hat{I}_{-(A)} + \hat{I}_{-(B)} | \Psi_i \rangle.$$

Now calculate the value of the right hand side of this expression for the six potential absorptions: $\Psi_i = \phi_1 \rightarrow \Psi_f = \phi_2$ and similarly $\phi_1 \rightarrow \phi_3$, $\phi_1 \rightarrow \phi_4$, $\phi_2 \rightarrow \phi_3$, $\phi_2 \rightarrow \phi_4$, and finally $\phi_3 \rightarrow \phi_4$.

You should find that two transitions are forbidden and four are allowed:

$$\begin{aligned} (\mathbf{R}_{12})_x &\propto \cos \theta + \sin \theta \\ (\mathbf{R}_{23})_x &\propto 0 \\ (\mathbf{R}_{13})_x &\propto -\sin \theta + \cos \theta \\ (\mathbf{R}_{24})_x &\propto \cos \theta + \sin \theta \\ (\mathbf{R}_{14})_x &\propto 0 \\ (\mathbf{R}_{34})_x &\propto -\sin \theta + \cos \theta. \end{aligned}$$

Draw in the four allowed transitions on your energy level diagram, and calculate the observable transition frequencies. You should find

$$\nu_{12} \equiv \frac{E_2 - E_1}{h} = \nu_0 \left(1 - \frac{\sigma_A + \sigma_B}{2} \right) + \frac{D}{2h} - \frac{J}{2}$$

$$\nu_{13} \equiv \frac{E_3 - E_1}{h} = \nu_0 \left(1 - \frac{\sigma_A + \sigma_B}{2} \right) - \frac{D}{2h} - \frac{J}{2}$$

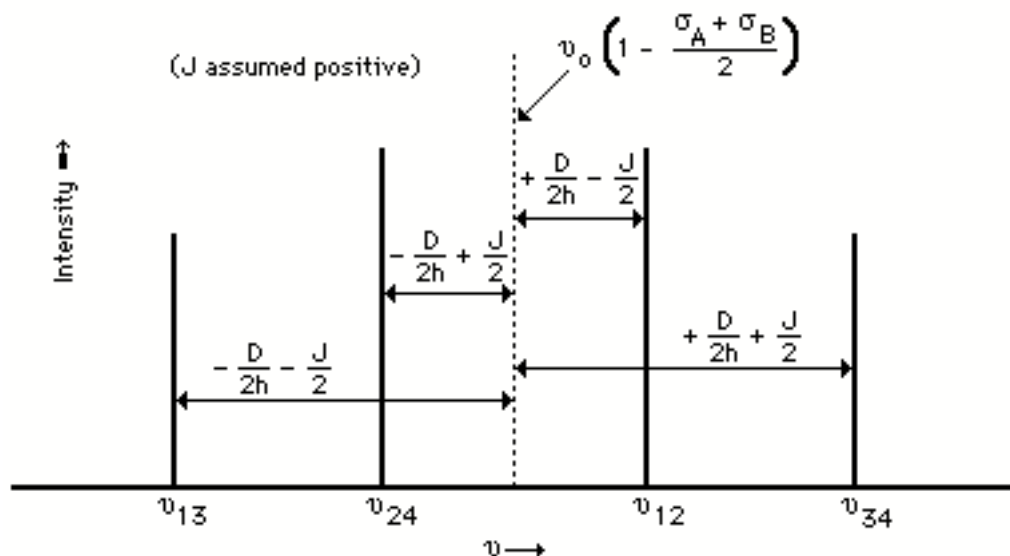
$$\nu_{24} \equiv \frac{E_4 - E_2}{h} = \nu_0 \left(1 - \frac{\sigma_A + \sigma_B}{2} \right) - \frac{D}{2h} + \frac{J}{2}$$

$$\nu_{34} \equiv \frac{E_4 - E_3}{h} = \nu_0 \left(1 - \frac{\sigma_A + \sigma_B}{2} \right) + \frac{D}{2h} + \frac{J}{2}$$

where $D/2$ was defined earlier (in the expression for E_{\pm}) as

$$\frac{D}{2} = \left[\left(\frac{h\nu_0\delta}{2} \right)^2 + \left(\frac{hJ}{2} \right)^2 \right]^{1/2}.$$

The first term in each of the transition frequency expressions is, of course, the overwhelmingly large one, being very nearly 1.21×10^8 Hz in every phosphorus NMR experiment conducted on the Varian 300 MHz NMR Spectrometer. The $D/2h$ and $J/2$ terms are very small in comparison, each on the order of tens of Hz. Noticing that $D/2$ can never be less than $hJ/2$, we can easily draw a typical AB spectrum, as shown below. The spectrum is centered about the frequency $\nu_0 [1 - (\sigma_A + \sigma_B)/2]$.



The relative intensity pattern can be calculated by comparing the squared values of $(R_{if})_x$. These can be written in very simple form with the help of the trigonometric identity

$$\sin 2\theta = 2 \sin \theta \cos \theta.$$

Using this identity we find, with I standing for intensity,

$$I_{12} \propto 1 + \sin 2\theta$$

$$I_{24} \propto 1 + \sin 2\theta$$

$$I_{13} \propto 1 - \sin 2\theta$$

$$I_{34} \propto 1 - \sin 2\theta$$

The only remaining point is the evaluation of $\sin 2\theta$ in terms of the experimental parameters δ , J , and ν_0 . The required expression for $\sin 2\theta$ is implicitly at hand because we have an expression for $\tan \theta$ in terms of integrals which we have already evaluated. One way to proceed is simply to develop a trigonometric identity relating $\sin 2\theta$ and $\tan \theta$; such a head-on approach produces relatively tedious algebra but will work. A less direct assault has merit. Going back to the secular equation from which we found \mathbf{c}_+ and \mathbf{d}_+ , one may use the expression for E_+ (in terms of integrals and D) to write:

$$\frac{\mathbf{c}_+}{\mathbf{d}_+} = \frac{\cos \theta}{\sin \theta} = \cot \theta = \frac{-H_{33} + H_{22} + D}{2H_{32}}.$$

One may now subtract this expression for $\cot \theta$ from the similar one for $\tan \theta$ to eliminate D :

$$\tan \theta - \cot \theta = \frac{H_{33} - H_{22}}{H_{32}}.$$

Writing $\tan \theta$ and $\cot \theta$ in terms of $\sin \theta$ and $\cos \theta$, clearing fractions, and using a couple of double angle formulas one may write:

$$\frac{-2 \cos 2\theta}{\sin 2\theta} = \frac{H_{33} - H_{22}}{H_{32}}.$$

Squaring and adding 1 to both sides yields, after simplification:

$$\sin^2 2\theta = \frac{4H_{32}^2}{(H_{33} - H_{22})^2 + 4H_{32}^2}.$$

Noticing that the denominator is just D^2 we may finally write:

$$\sin 2\theta = \frac{2H_{32}}{D} = \frac{hJ}{[(h\nu_0 \delta)^2 + (hJ)^2]^{1/2}}.$$

Thus the intensity ratios may be calculated from the measured quantities J and δ and compared with the experimental ratios.

We can now simulate the spectrum for arbitrary values of J and δ . Such a simulation is very useful in showing how the spectrum looks at various limits: $J \gg \nu_0\delta$, $J \ll \nu_0\delta$, or $J \approx \nu_0\delta$. Such a simulation is available through the course web site page for this experiment. This simulation plots the full spectrum along with a close-up view of that portion of the spectrum at frequencies above the spectrum center for arbitrary J and δ values of your choosing. These spectra are shown against a relative frequency axis, $\Delta\nu$, which measures the frequency shift from the spectrum's center.

Summary Of Required Calculations

1) Successful completion of the calculations outlined to this point will be counted about one-half towards your grade for this experiment. If you are unable to complete a particular calculation, use the intermediate results in the handout and go on to the next. With these intermediate results, you may do most parts of the calculation independently. This calculation is to be viewed as an open-book, open-notes, take-home exam (but worth only about half a lab)—your work is expected to be an independent effort except for possible help from an instructor. The calculations can be done in pencil and attached as an appendix to the rest of the lab report.

2) The remaining part of the lab may be completed without having done any of the calculations. The experimental spectrum you have obtained contains a central set of four lines—the AB pattern similar to the “stick” spectrum shown on page 9—and some additional signals both to low, and to high field of the central AB quartet. For the central AB quartet, calculate distances between appropriate transitions in order to get at least two independent values of J and of D/h (in Hz). Use the differences in measured values to assign a rough uncertainty to the mean values of J and of D/h .

3) Taking $\nu_0 = 121.426 \times 10^6$ Hz, use the mean values of J and D/h to calculate a value for δ , the relative chemical shift.

4) Recalling that $\sin 2\theta = hJ/D$, use the mean value of J and D/h to calculate the expected relative intensities. Compare the “theoretical” intensity ratios with the experimental ratios.

Discussion

Using the transition frequency and the relative intensity relationships previously derived, it is possible to construct typical spectra for different relative values of J and δ . Draw representative spectra which illustrate the following molecular situations for a system of two phosphorus nuclei using the web site simulator for guidance.

1) $J = 0, \delta \neq 0$. The phosphorus nuclei A and B, while chemically different, are uncoupled.

2) $J \ll \nu_0\delta$. The phosphorus-phosphorus coupling is so small compared to the relative chemical shift that first order energy calculations are sufficient.

3) The case $J \approx \nu_0\delta$ produces a spectrum similar to the one you have analyzed and you need not illustrate it, but you may want to compare your spectrum to the program's output for this case.

4) $J \gg \nu_0\delta$. This is the case of strong phosphorus-phosphorus coupling or perhaps a very small relative chemical shift—almost equivalent phosphorus nuclei.

5) $\delta = 0, J \neq 0$. The appearance of this spectrum illustrates why it is that even strongly coupled but chemically equivalent nuclei fail to "split" one another.

6) J may be either positive or negative. How would a negative value of J affect the appearance of the typical spectra you have constructed?

As mentioned previously, the experimental spectrum you obtained contained not only the central AB pattern that you have already analyzed, but some additional signals both to low, and to high field of the central AB quartet. The remainder of this exercise involves explaining why these additional signals occur with the patterns you observed. The origin of these additional signals can be traced to the fact that Pt exists as a mixture of isotopes, the most abundant (~33%) of which is ^{195}Pt . All the isotopes of Pt, except for ^{195}Pt , have nuclear spin quantum numbers $I = 0$, and the AB spectrum you have analyzed (the central set of four lines) is produced by the molecules in the sample which do NOT contain ^{195}Pt .

However, ^{195}Pt has a nuclear spin quantum number $I = 1/2$ and will couple with other nuclei having non-zero I values—e.g., ^{31}P nuclei. The additional signals in your spectrum are therefore due to the approximately 33% of the molecules which contain ^{195}Pt . These latter signals are called **satellites**.

Since the chemical shift of ^{195}Pt (64.49 MHz at the magnetic field strengths used in your experiment) is very different from that of ^{31}P (121.426 MHz), the chemical shift difference δ is very large, and the nuclear spin-spin coupling constant $J_{\text{Pt P}} \ll \delta$. Thus, the effect of the presence of ^{195}Pt on the ^{31}P spectrum can be determined using a “first-order” analysis, i.e., the approach we followed in building up the NMR spectrum of HF. Here it is important to emphasize that since $^{31}\text{P}_\text{A}$ and $^{31}\text{P}_\text{B}$ are in different chemical environments, they will have, in principle, different coupling constants to ^{195}Pt .

7) Examine the relative intensities of the low field pattern (i.e., the low field satellite), and compare them with those that you measured for the central AB quartet you have already analyzed. From this examination and a consideration of the results of the simulations you performed in 2) and 3) above, do you conclude that the “effective” chemical shift difference, δ , between $^{31}\text{P}_\text{A}$ and $^{31}\text{P}_\text{B}$ for this **low** field group of lines arising from molecules containing ^{195}Pt is LARGER or SMALLER than that found in your analysis of the central AB quartet? Explain how this has arisen, and determine the relative magnitudes of J_{PtP_A} and J_{PtP_B} . Is $J_{\text{PtP}_\text{A}} > J_{\text{PtP}_\text{B}}$ or is $J_{\text{PtP}_\text{A}} < J_{\text{PtP}_\text{B}}$?

8) Examine the relative intensities of the high field satellite and compare them with those that you measured for the central AB quartet you have already analyzed. From this examination and a consideration of the results of the simulations you performed in 4) and 5) above, do you conclude that the “effective” chemical shift difference δ between $^{31}\text{P}_\text{A}$ and $^{31}\text{P}_\text{B}$ for this **high** field group of lines arising from molecules containing ^{195}Pt is LARGER or SMALLER than that found in your analysis of the central AB quartet? Explain how this has arisen. Is your explanation consistent with the relative magnitudes of J_{PtP_A} and J_{PtP_B} you determined in 7)?

9) Use your answers to 7) and 8) and the full spectrum you measured (i.e., the low field lines, the central AB quartet, and the high field lines) to calculate a numerical value for $|J_{\text{PtP}_\text{B}} - J_{\text{PtP}_\text{A}}|$.

References

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