

# An Experimental Study of Isotope Effects on NMR Parameters in the Solid State

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We report on a variety of systems for which it has been possible to measure intrinsic isotope effects on the chemical shielding (the *isotope shift*) in the solid state. The spin systems investigated are  $^{11}\text{B}(^{2/1}\text{H})$ ,  $^{13}\text{C}(^{2/1}\text{H})$ ,  $^{15}\text{N}(^{2/1}\text{H})$ ,  $^{31}\text{P}(^{2/1}\text{H})$ ,  $^{95}\text{Mo}(^{13/12}\text{C})$ , and  $^{199}\text{Hg}(^{13/12}\text{C})$ . The results agree well with data available from solution NMR studies.

## 1. Introduction

The effects of isotopic substitution on the NMR chemical shift and scalar part of the indirect spin–spin coupling have been extensively studied for many years; reviews cover both experimental results<sup>1</sup> and theoretical aspects.<sup>2</sup> However, the vast majority of previous experimental studies have been on either gas- or liquid-phase samples. The terms *intrinsic* isotope effect and *equilibrium* isotope effect have been used to distinguish between two extreme types of isotope effects on the chemical shift.<sup>3</sup> The former refers to the effects of rovibrational averaging on a single species that does not undergo conformational or chemical exchange; the vibrational potential energy surface in such systems is thus expected to be single-minimum in nature. The latter term describes the effects due to population changes of two or more species in systems that undergo a rapid exchange equilibrium; such systems are characterized by potential energy surfaces with multiple minima. Compared to these two extreme cases, the description of intermediate-type systems (e.g. strongly hydrogen-bonded systems<sup>4</sup>) may become complicated by the presence of both intrinsic and equilibrium effects.

Although isotope effects on chemical shielding have been observed in the solid state as an important technique in the investigation of low-barrier hydrogen bonds,<sup>5,6</sup> we know of only one previous study in which specifically intrinsic isotope effects have been observed via solid-state NMR: Benedict et al.<sup>6</sup> measured the effects of one-bond deuterium substitution on the  $^{15}\text{N}$  isotropic chemical shift of hydrogen bis(isocyanide) salts; their results were discussed in terms of low-barrier hydrogen bonds. Although the authors did not discuss their results explicitly in terms of intrinsic isotope effects, their observation of two distinct resonances (for the compound pair **1e** and **1f**) indicates that equilibrium isotope effects are not operative. Rather, the large magnitudes of the isotope shifts (3–4 ppm), and the authors' successful theoretical modeling of the observations, show that intermolecular effects can have a dramatic influence on intrinsic isotope effects. We report here a collection of general observations of intrinsic isotope effects in solid-state NMR and compare the results with data available for liquid-state solution systems. Our goals were 2-fold: (1) to sample a variety of  $\text{A},^{m'/m}\text{X}$  spin pair systems to see how readily isotope effects could be observed and (2) to compare

the results with those from solution systems as a test of the underlying theory that is expected to be valid regardless of the physical state of the system. The particular compounds were chosen because they represent a wide variety of spin systems, were known or expected to have relatively narrow line widths in the solid state, and were readily available.

It would be, in principle, preferable to measure the isotope effects upon the chemical shift tensor elements, as they inherently contain more information about the chemical environment of the observed nucleus than does the isotropic chemical shift. However, the greater experimental error associated with determining the tensor elements may limit the number of systems for which such effects could be observed. To our knowledge, the work of Lagier et al.<sup>5</sup> is the only successful study of this type. We follow the sign convention introduced by Gombler<sup>7</sup> and the notation of Jameson<sup>2</sup> in using the definition

$$\begin{aligned} {}^n\Delta\text{A}(^{m'/m}\text{X}) &= \sigma_{\text{A}} - \sigma_{\text{A}}^* \\ &= \delta_{\text{A}}^* - \delta_{\text{A}} \end{aligned} \quad (1)$$

to describe the so-called *isotope shift* of nucleus A due to the replacement of nuclide  $^m\text{X}$  with the more massive  $^{m'}\text{X}$ . The asterisk on  $\sigma_{\text{A}}$  (absolute chemical *shielding*) and  $\delta_{\text{A}}$  (relative chemical *shift*) indicates the system with the larger mass. The letter  $n$  indicates the number of intervening bonds between nuclei A and X. Several trends are typically observed for isotope shifts and bear a close relationship to theoretical considerations:<sup>1c</sup>

(i) Substitution by a heavier nuclide ( $m' > m$ ) generally results in greater shielding of A. Consequently, isotope shifts are generally negative according to the sign convention of eq 1.

(ii) The greater the relative change in mass, the greater the isotope shift.

(iii) The isotope shift is approximately additive; specifically, it is approximately proportional to the number of isotopically substituted, chemically equivalent atoms.

(iv) Nuclei having large chemical shielding ranges show greater isotope shifts.

(v) The magnitude of the isotope shift decreases as the number of intervening bonds increases.

We use the definition of Jameson<sup>8</sup> to describe the primary isotope effect on the  $n$ -bond spin–spin coupling,  ${}^nJ(\text{A},\text{X})$ :

$$\Delta_p^n J(\text{A},^{m'/m}\text{X}) = \left( \frac{\gamma_{m'\text{X}}}{\gamma_{m\text{X}}} \right) |{}^nJ(\text{A},^{m'}\text{X})| - |{}^nJ(\text{A},^m\text{X})| \quad (2)$$

## 2. Experimental Section

Solid-state NMR spectra were obtained on Bruker MSL-200 ( $B_0 = 4.7$  T) and AMX-400 ( $B_0 = 9.4$  T) spectrometers, using

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TABLE 1: Isotope Shift Data<sup>a</sup> for Several Solid- and Solution-State Samples

system	A	<i>m'</i> / <i>m</i> X	<i>n</i>	<sup>n</sup> ΔA( <i>m'</i> / <i>m</i> X)/ppm		<sup>1</sup> J(A, <i>m'</i> X)/Hz		remarks
				solid	solution	solid	solution	
NaBH <sub>4</sub>	<sup>11</sup> B	<sup>2</sup> / <sub>1</sub> H	1	−0.60(2)	−0.58(4) <sup>b</sup>			
	<sup>11</sup> B	<sup>2</sup> / <sub>1</sub> H	1		−0.543(7) <sup>c</sup>			
adamantane	<sup>13</sup> C	<sup>2</sup> / <sub>1</sub> H	1 <sup>d</sup>	−1.28	−1.22 <sup>e</sup>	19.8(2)	20.18(6) <sup>e</sup>	CH carbon
	<sup>13</sup> C	<sup>2</sup> / <sub>1</sub> H	1 <sup>d</sup>	−1.37	−1.32 <sup>e</sup>	19.0(9)	19.36(8) <sup>e</sup>	CH <sub>2</sub> carbon
NH <sub>4</sub> Cl	<sup>15</sup> N	<sup>2</sup> / <sub>1</sub> H	1	−1.64	−1.30 <sup>f</sup>	−10.5(7)	−11.25(2) <sup>g</sup>	N <sup>2</sup> H <sub>4</sub> Cl
phthalimide	<sup>15</sup> N	<sup>2</sup> / <sub>1</sub> H	1	−0.84(5)		14.5		4.7 T
	<sup>15</sup> N	<sup>2</sup> / <sub>1</sub> H	1		−0.78(2)			9.4 T
P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	<sup>31</sup> P	<sup>2</sup> / <sub>1</sub> H	3–5 <sup>h</sup>	−0.67	−0.67 <sup>i</sup>			
phenylphosphinic acid	<sup>31</sup> P	<sup>2</sup> / <sub>1</sub> H	1		−0.407(1) <sup>j</sup>		86.3(1) <sup>j</sup>	
Mo(CO) <sub>6</sub>	<sup>95</sup> Mo	<sup>13</sup> / <sub>12</sub> C	1	−0.316 <sup>k</sup>	−0.316(8)	69(1) <sup>k</sup>	68.4(2)	( <sup>13</sup> CO) <sub>1</sub> ( <sup>12</sup> CO) <sub>5</sub>
K <sub>2</sub> Hg(CN) <sub>4</sub>	<sup>199</sup> Hg	<sup>13</sup> / <sub>12</sub> C	1	+0.27		1512		( <sup>13</sup> CN) <sub>1</sub> ( <sup>12</sup> CN) <sub>3</sub>
N(Et) <sub>4</sub> Na[Hg(CN) <sub>4</sub> ]	<sup>199</sup> Hg	<sup>13</sup> / <sub>12</sub> C	1	+0.27(5)		1530(2)		( <sup>13</sup> CN) <sub>1</sub> ( <sup>12</sup> CN) <sub>3</sub>
	<sup>199</sup> Hg	<sup>13</sup> / <sub>12</sub> C	1	+0.60(5)		1529(2)		( <sup>13</sup> CN) <sub>2</sub> ( <sup>12</sup> CN) <sub>2</sub>

<sup>a</sup> Experimental uncertainties in the least significant digit, where known, are indicated in parentheses. <sup>b</sup> In basic, aqueous solution.<sup>9</sup> <sup>c</sup> In basic, aqueous solution.<sup>10</sup> <sup>d</sup> In addition to the one-bond isotope shifts, multiple-bond effects are also present, due to the full deuteration of the molecule. <sup>e</sup> With CDCl<sub>3</sub> as solvent. <sup>f</sup> Median and average value of <sup>1</sup>Δ<sup>14</sup>N(<sup>2</sup>/<sub>1</sub>H) for a series of seven NH<sub>4</sub>Cl solutions;<sup>15</sup> the range is 0.06 ppm. <sup>g</sup> Solution was 4 M NH<sub>4</sub>NO<sub>3</sub> in 2 M HCl(aq).<sup>16</sup> <sup>h</sup> Full deuteration resulted in values of *n* = 3(6), *n* = 4(6), and *n* = 5(3). <sup>i</sup> With CH<sub>2</sub>Cl<sub>2</sub> as solvent. <sup>j</sup> Solution was ≈1.7 M phenylphosphinic acid in methanol-*d*<sub>1</sub>. <sup>k</sup> From ref 23.

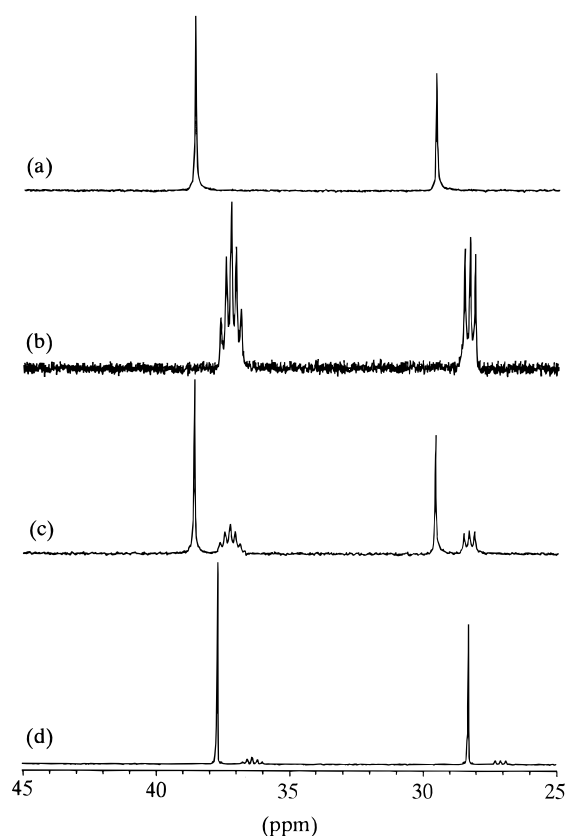
magic-angle spinning (MAS), with proton cross-polarization (CP) and decoupling for samples containing <sup>1</sup>H. Solution-state spectra were obtained on Bruker AC-250 (*B*<sub>0</sub> = 5.9 T) or AMX-400 spectrometers. Chemical shifts for <sup>13</sup>C were externally referenced to TMS. Nitrogen-15 chemical shifts were externally referenced to solid <sup>15</sup>NH<sub>4</sub>NO<sub>3</sub> and are reported with respect to liquid ammonia at 20 °C, which is 23.8 ± 0.3 ppm more shielded than ammonium nitrate. Phosphorus-31 chemical shifts are reported with respect to 85% H<sub>3</sub>PO<sub>4</sub> solution at 20 °C, using solid NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (*δ*<sub>iso</sub> = +0.81 ppm) as a secondary reference for measurements of solids. Solution samples of adamantane and Mo(CO)<sub>6</sub> were prepared in CDCl<sub>3</sub>. Phthalimide, triphenylphosphine, and phenylphosphinic acid solution samples were prepared in DMSO, CH<sub>2</sub>Cl<sub>2</sub>, and methanol-*d*<sub>1</sub>, respectively.

### 3. Results and Discussion

The systems for which solid-state isotope shifts have been observed are reported below, categorized according to the observed and isotopically substituted nuclei. All experimental data are collected in Table 1.

**<sup>1</sup>Δ<sup>11</sup>B(<sup>2</sup>/<sub>1</sub>H): Sodium Borohydride.** The <sup>11</sup>B MAS NMR spectra of fully protonated and fully deuterated sodium borohydride, NaBH<sub>4</sub>, were acquired at 9.4 T via a one-pulse sequence with proton decoupling and a sample-spinning rate of 10 kHz. The isotope shift was observed to be <sup>1</sup>Δ<sup>11</sup>B(<sup>2</sup>/<sub>1</sub>H) = −0.60 ± 0.01 ppm. This value compares with previously reported solution-state isotope shifts of −0.58 ± 0.04<sup>9</sup> and −0.543 ± 0.007 ppm,<sup>10</sup> both of which are for fully deuterated NaBH<sub>4</sub> in basic, aqueous solution. The solid-state isotope shift thus appears to be as much as 10% greater in magnitude than values obtained from solution studies. From the resolution-enhanced <sup>11</sup>B MAS NMR spectrum of the fully deuterated sample, <sup>1</sup>J(<sup>11</sup>B,<sup>2</sup>H) = 12.5 Hz was estimated; this value is in agreement with <sup>1</sup>J(<sup>11</sup>B,<sup>1</sup>H) = 80.6<sup>10</sup> and 81.00 Hz<sup>11</sup> when account is taken of the ratio *γ*<sub>H</sub>/*γ*<sub>B</sub> = 6.514<sup>12</sup> (see eq 2).

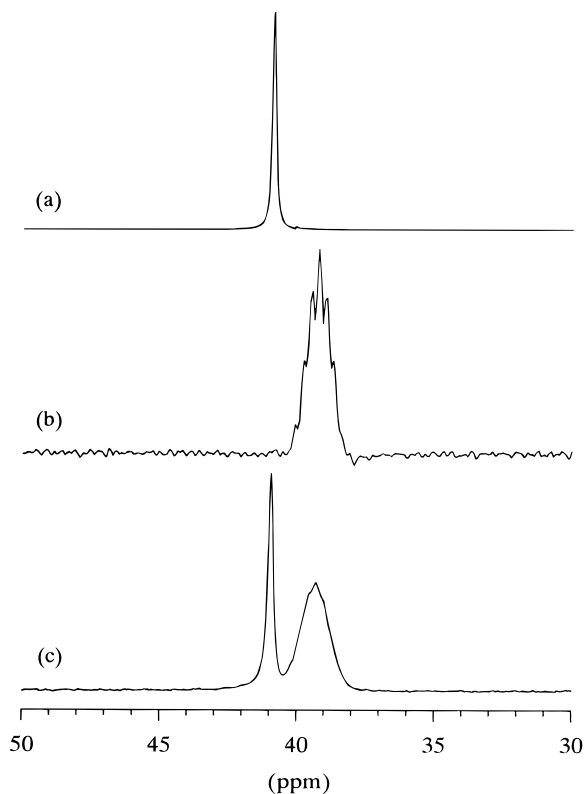
**<sup>n</sup>Δ<sup>13</sup>C(<sup>2</sup>/<sub>1</sub>H): Adamantane.** The <sup>13</sup>C MAS NMR spectra of adamantane and adamantane-*d*<sub>16</sub> are shown in parts a and b of Figure 1 respectively. The narrow line widths (≈7 Hz) observed in Figure 1b indicate that intermolecular dipole–dipole interactions are effectively removed by rapid sample rotation. The multiplet structures in Figure 1b–d result from the <sup>13</sup>C–<sup>2</sup>H spin–spin coupling, <sup>1</sup>J(<sup>13</sup>C,<sup>2</sup>H), in the CD<sub>2</sub> and CD groups. The isotope effect on the <sup>13</sup>C chemical shift is clearly observable. Figure 1c shows the <sup>13</sup>C MAS spectrum of a solid-state mixture of adamantane and adamantane-*d*<sub>16</sub>. For comparison of the



**Figure 1.** <sup>13</sup>C NMR spectra of adamantane: (a) CP MAS NMR spectrum of the protonated solid; (b) MAS NMR spectrum of the fully deuterated solid; (c) MAS NMR spectrum of a mixture of the protonated and deuterated solid; (d) NMR spectrum of a mixture of protonated and deuterated adamantane in CDCl<sub>3</sub> solution. All solid-state MAS spectra were recorded at *B*<sub>0</sub> = 9.4 T, using a sample-spinning frequency of 6500 Hz, a recycle delay of 60 s, and coaddition of 16 transients.

isotope effects in the solid and solution states, Figure 1d shows the <sup>13</sup>C spectrum of a mixture of adamantane and adamantane-*d*<sub>16</sub> in solution with CDCl<sub>3</sub> as solvent. Comparison of parts c and d of Figure 1 illustrates the overall chemical shift change between the solid- and solution-phase systems; such changes may reflect differences in both intermolecular effects and bulk magnetic susceptibility between the solid and solution media.

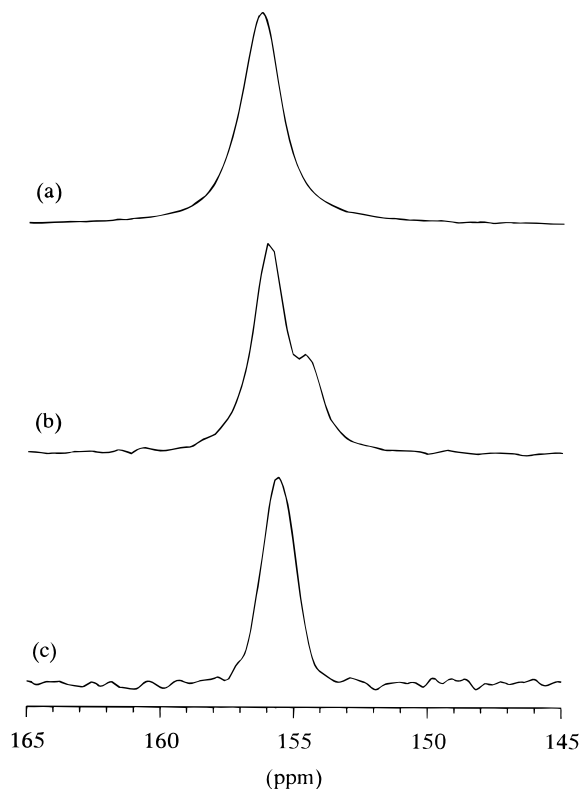
The total isotope shift in the solid is −1.28 and −1.37 ppm for the CH and CH<sub>2</sub> carbon nuclei, respectively; in solution,



**Figure 2.** (a)  $^{15}\text{N}$  CP MAS NMR spectrum of  $^{15}\text{NH}_4\text{Cl}$ ; sample-spinning frequency is 1726 Hz. (b) The resolution-enhanced,  $^{15}\text{N}$  MAS NMR spectrum of  $^{15}\text{ND}_4\text{Cl}$ ; sample-spinning frequency is 5256 Hz. (c) The  $^{15}\text{N}$  MAS NMR spectrum of a mixture of  $^{15}\text{NH}_4\text{Cl}$  and  $^{15}\text{ND}_4\text{Cl}$ ; sample-spinning frequency is 5256 Hz. All spectra were recorded at  $B_0 = 9.4$  T, using a recycle delay of 30 s and coaddition of 16 transients.

the respective isotope shifts are  $-1.22$  and  $-1.32$  ppm, thus indicating that the isotope shifts are of about 4% greater magnitude in the solid state. Values of  $^1\Delta^{13}\text{C}(^2\text{H})$  and  $^1J(^{13}\text{C}, ^2\text{H})$  for both solid and solution spectra are given in Table 1. The study reported here involved only the fully deuterated compound; therefore, we are unable to comment on the substituent components of the total isotope shift, specifically the individual one-bond, two-bond, etc. contributions. However, Majerski et al.<sup>13</sup> have reported a detailed analysis of isotope effects for protoadamantane; their findings are in agreement with general observations, for example additivity and decreasing magnitude with increasing  $n$ .

**$^1\Delta^{15}\text{N}(^2\text{H})$ : Ammonium Chloride and Phthalimide.** The  $^{15}\text{N}$  CP MAS NMR spectrum of  $^{15}\text{NH}_4\text{Cl}$  is shown in Figure 2a. A single peak of 6 Hz line width is observed at 40.96 ppm. Figure 2b shows the resolution-enhanced  $^{15}\text{N}$  resonance of  $^{15}\text{ND}_4\text{Cl}$ , which is more shielded than that of  $^{15}\text{NH}_4\text{Cl}$ ; from this spectrum,  $^1J(^{15}\text{N}, ^2\text{H})$  was determined to be  $-10.5$  Hz (with the negative sign being presumed rather than observed<sup>14</sup>). The  $^{15}\text{N}$  MAS NMR spectrum of a mixture of  $^{15}\text{NH}_4\text{Cl}$  and  $^{15}\text{ND}_4\text{Cl}$  is shown in Figure 2c. The solid-state isotope shift of  $-1.64$  ppm compares with  $^1\Delta^{14}\text{N}(^2\text{H})$  in the range  $-1.24$  to  $-1.36$  ppm<sup>15</sup> for a series of ammonium chloride solutions of varying concentration and pH. The approximately 25% increase in magnitude of the isotope shift in the solid state (as compared to solution-state values) is not unreasonable in view of the considerable sensitivity to counterion, concentration, and pH, as observed for isotope shifts of nitrogen in ammonium compounds.<sup>15</sup> Figure 3 illustrates the  $^{15}\text{N}$  MAS NMR spectra of solid phthalimide. In contrast to  $\text{NaBH}_4$ , adamantane, and ammonium chloride, which are partially rotationally mobile in



**Figure 3.**  $^{15}\text{N}$  MAS NMR spectra of phthalimide- $^{15}\text{N}$ : (a) Protonated phthalimide at  $B_0 = 4.7$  T; 24 transients. (b) Deuterated phthalimide at  $B_0 = 4.7$  T; 32 transients. (c) Deuterated phthalimide at  $B_0 = 9.4$  T; 100 transients.

the solid state at room temperature,<sup>17</sup> phthalimide is a typical, rigid organic solid.<sup>18</sup> The line width of the proton-decoupled  $^{15}\text{N}$  CP MAS spectrum obtained at  $B_0 = 4.7$  T is 31 Hz as shown in Figure 3a. For deuterated phthalimide at  $B_0 = 4.7$  T, an asymmetric doublet with a splitting of 29 Hz is observed in the MAS spectrum, as shown in Figure 3b. This asymmetric doublet results from residual dipolar coupling of  $^2\text{H}$  to  $^{15}\text{N}$  as a consequence of the quadrupolar  $^2\text{H}$  nuclear spins not being quantized exactly along  $B_0$ , and thus magic-angle spinning does not fully average the direct  $^2\text{H}$ – $^{15}\text{N}$  dipolar interaction to zero.<sup>19</sup> A perturbative treatment of this phenomenon is valid when, for the quadrupolar nucleus, the Zeeman interaction is much larger than the quadrupolar interaction ( $\hat{H}_Z \gg \hat{H}_Q$ ).

The effect of residual dipolar coupling on the spin- $1/2$  ( $I$ ) MAS spectrum is to alter the positions of the  $2S + 1$  peaks according to

$$\nu_{m_S}(I) = \nu_{\text{iso}}(I) - m_S J_{IS} + \left( \frac{3D'\chi}{20\nu_S} \right) \left[ \frac{S(S+1) - 3m_S^2}{S(2S-1)} \right] f(\alpha, \beta, \eta) \quad (3)$$

where  $\nu_{\text{iso}}(I)$  is the isotropic  $I$ -spin resonance frequency in Hz,  $m_S$  are the  $S$ -spin magnetic quantum numbers, and  $J_{IS}$  is the scalar part of the indirect spin–spin coupling tensor. The Larmor frequency and quadrupolar coupling constant ( $e^2qQ/h$ ) of the  $S$ -spin are given by  $\nu_S$  and  $\chi$ , respectively. The direct dipolar coupling and the anisotropy in the indirect coupling are given by the first and second terms, respectively, on the right-hand side of eq 4

$$D' = D - \Delta J_{IS}/3 \quad (4)$$

with the direct dipolar parameter, in Hz:

$$D = \left( \frac{\mu_0}{4\pi} \right) \left( \frac{\gamma_I \gamma_S \hbar}{2\pi r_{IS}^3} \right) \quad (5)$$

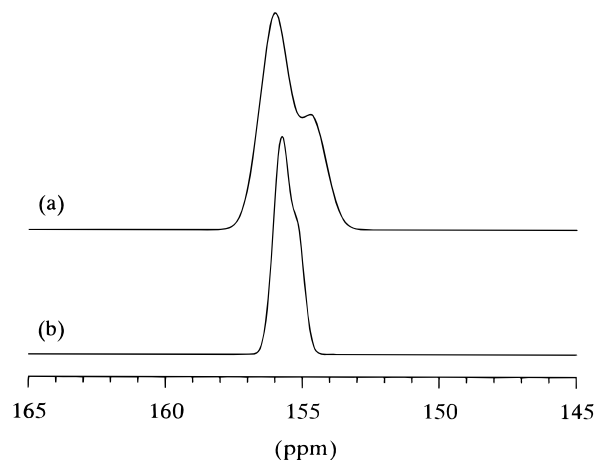
The function  $f(\alpha, \beta, \eta)$  depends on the angles  $(\alpha, \beta)$  defining the relative orientation of the dipolar and quadrupolar coupling tensors, and on the quadrupolar coupling asymmetry parameter,  $\eta$ .<sup>19</sup>

It can be shown<sup>21</sup> that for the case of  $S = 1$ , the two lines corresponding to  $m_S = \pm 1$  of the  $I$ -spin MAS spectrum are perturbed in a sense opposite to—and each by an amount equal to half the magnitude of—that of the  $m_S = 0$  line, as a function of the ratio  $(3D\chi)/(20\nu_S)$ . The overall sense of the perturbations depends only on the sign of  $\chi$ :<sup>19</sup> if  $\chi > 0$ , the  $m_S = \pm 1$  lines shift to lower frequency and the  $m_S = 0$  line to higher frequency. Thus, the frequency separation between the lines corresponding to  $m_S = \pm 1$  is equal to  $2J_{IS}$ . The  $m_S = 0$  line and one of the  $m_S = \pm 1$  lines will coincide when  $|J_{IS}| = |(9D\chi)/(10\nu_S)|$  resulting in a doublet of 2:1 intensity ratio. From eq 3, it can be seen that a 1:2 doublet results also in the event that  $J_{IS} = 0$ ; however, in this case the sense of the doublet is reversed, provided the sign of  $\chi$  is the same. The isotropic frequency of the  $I$ -spin resonance is given, in all cases, by the weighted average of the sum of the individual line positions in the MAS spectrum:

$$\nu_{\text{iso}}(I) = (2S + 1)^{-1} \sum_{m_S} \nu_{m_S}(I) \quad (6)$$

Within experimental error, the 29 Hz splitting of the observed 2:1  $^{15}\text{N}$  doublet (Figure 3b) indicates  $^1J(^{15}\text{N}, ^2\text{H}) = -14.5$  Hz, which agrees with the value of  $-14.3$  Hz obtained using  $^1J(^{15}\text{N}, ^1\text{H}) = -93.0 \pm 0.8$  Hz<sup>20</sup> and  $\gamma^1\text{H}/\gamma^2\text{H}$ <sup>12</sup> (again, the signs are presumed to be negative<sup>14</sup>). For the  $^{15}\text{N}$ – $^2\text{H}$  system in phthalimide, we neglect the  $\Delta J_{IS}$  term owing to the small value of  $J_{\text{NH}}$ . Further, the quadrupolar coupling tensor is expected to be coincident with the internuclear vector and to be approximately axially symmetric, resulting in  $f(\alpha, \beta, \eta) = 2$ .

A comparison of  $\nu_{\text{iso}}(^{15}\text{N})$  for the protonated and deuterated samples at 4.7 T (see Figure 3a,b), using eq 6 for the latter, indicates an isotope shift of  $-0.84 \pm 0.05$  ppm. From the deuterated sample spectrum acquired at 9.4 T (Figure 3c), the apparent isotope shift is found to be  $-0.68$  ppm when the (single) peak maximum is taken to represent  $\nu_{\text{iso}}(I)$ . As described below, this value represents a lower limit (in magnitude) of the true isotope shift. The nonequivalence of the isotope shifts deduced from experimental spectra at 4.7 and 9.4 T is a consequence of the combination of a relatively broad natural line width, the magnitudes of  $D\chi/\nu_S$  and  $J_{IS}$ , and the residual dipolar effects not being eliminated at the greater magnetic field. It is fortuitous that the relevant parameters ( $\Delta\nu_{1/2}$ ,  $^1J(^{15}\text{N}, ^2\text{H})$ ,  $D\chi/\nu_S$ ) have values such that, at 4.7 T, the central  $^{15}\text{N}$  peak is approximately coincident with the outer, high-frequency peak. These circumstances provide maximal (i.e.,  $2J_{IS}$  for the case in which  $J_{IS}$  is greater than the third term on the right-hand side of eq 3) but barely sufficient resolution of the maxima of the three peaks. At 9.4 T, this optimal resolution is lost due to the noncoincidence of the two peaks and the subsequent loss of separation between the two high-frequency peaks and the low-frequency peak. The result is the inability to clearly determine any of the  $\nu_{m_S}$  and hence  $\nu_{\text{iso}}(I)$ . Specifically, the frequency of the (at 9.4 T, single) peak maximum is not an accurate representation of  $\nu_{\text{iso}}(I)$ . Theoretical calculations of the MAS spectrum at 4.7 and 9.4 T, as shown in Figure 4, indicate that this is indeed the case; therefore, the deduced isotope shift of  $-0.68$  ppm does not accurately



**Figure 4.** Calculated  $^{15}\text{N}$  MAS NMR spectra of deuterated phthalimide- $^{15}\text{N}$ : (a) at  $B_0 = 4.7$  T and (b) at  $B_0 = 9.4$  T. Parameters used were  $D = -1615$  Hz,  $^1J(^{15}\text{N}, ^2\text{H}) = 14.3$  Hz, and  $\chi = 310$  kHz.

represent the true value. This example illustrates the usefulness of acquiring spectra at different field strengths.

The  $^{15}\text{N}$  solution-state spectrum of a 1:1 mixture of phthalimide- $^{15}\text{N}, ^1\text{H}$ , and phthalimide- $^{15}\text{N}, ^2\text{H}$  in DMSO was recorded at 9.4 T. The isotope shift was observed to be  $-0.78 \pm 0.02$  ppm, which agrees well with the solid-state value of  $-0.84 \pm 0.05$  ppm. The complications arising from residual dipolar effects in the solid state prevent a more meaningful comparison between the solid- and solution-state isotope shifts for phthalimide. Because they had not previously observed  $^2\text{H}$  isotope effects on  $^{15}\text{N}$  chemical shifts in solids, Benedict et al.<sup>6</sup> concluded that "... $^1\Delta^{15}\text{N}(^2\text{H}) \neq 0$  is a criterion for the formation of a low-barrier hydrogen bond..." We have given two examples where this criterion is met; however, the results are entirely consistent with many existing data from gas- and liquid-phase studies and are satisfactorily consistent with intramolecular vibrational averaging effects. The significantly larger isotope effects reported by Benedict et al. (e.g., 3–4 ppm) agree quite nicely with their treatment of additional vibrational averaging effects of an intermolecular nature, thus indicating that one should be mindful about the possible importance of intermolecular effects. However, because of the possibility to observe intrinsic isotope shifts, we caution that  $^1\Delta^{15}\text{N}(^2\text{H}) \neq 0$  is not, in itself, sufficient evidence for the existence of a low-barrier hydrogen bond.

**$^{31}\text{P}(^2\text{H})$ : Triphenylphosphine and Phenylphosphinic Acid.** The  $^{31}\text{P}$  MAS spectra of triphenylphosphine,  $\text{P}(\text{C}_6\text{H}_5)_3$  and  $\text{P}(\text{C}_6\text{D}_5)_3$ , were recorded at  $B_0 = 4.7$  T with a sample-spinning frequency of 4050 Hz. The total  $^{31}\text{P}$  isotope shift in the solid state is  $-0.67$  ppm. A solution-state measurement of a mixture of  $\text{P}(\text{C}_6\text{H}_5)_3$  and  $\text{P}(\text{C}_6\text{D}_5)_3$  in  $\text{CH}_2\text{Cl}_2$  also resulted in a total isotope shift of  $-0.67$  ppm. In this case of full deuteration, as with adamantane- $d_{16}$ , it is not strictly possible to decompose the total, observed isotope shift into the different  $n$ -bond components. However, it has been shown<sup>22</sup> that for  $\alpha$ - $^{13}\text{C}$  nuclei bonded to phenyl groups (e.g., benzophenone), the  $^3\Delta^{13}\text{C}(^2\text{H})$  term is of approximately 3–4 times greater magnitude than either  $^4\Delta^{13}\text{C}(^2\text{H})$  or  $^5\Delta^{13}\text{C}(^2\text{H})$ , both of which are positive in sign.

The  $^{31}\text{P}$  CP MAS spectra of protonated and deuterated phenylphosphinic acid ( $\text{C}_6\text{H}_5\text{PHOOH}$  and  $\text{C}_6\text{H}_5\text{PDOOD}$ , respectively) were obtained at 9.4 T. The  $^{31}\text{P}$  isotropic chemical shift for the protonated species is  $19.66 \pm 0.02$  ppm. The apparent isotropic chemical shift for the deuterated species is  $19.50 \pm 0.02$  ppm, from which an isotope shift of  $^1\Delta^{31}\text{P}(^2\text{H}) = -0.16$  ppm results. However, broad lines are observed for

both systems: ca. 180 and 250 Hz, respectively, for the protonated and deuterated species. According to the previous discussion regarding the phthalimide- $^{15}\text{N}$ , $^2\text{H}$  system, residual dipolar effects may perturb the  $^{31}\text{P}$  spectrum of  $\text{C}_6\text{H}_5\text{PDOOD}$  in such a way as to preclude a meaningful measurement of the isotope shift. Further measurements of the  $\text{C}_6\text{H}_5\text{PDOOD}$  system at 4.7 T failed to provide sufficient separation of the peaks to allow a more meaningful experimental analysis. Line shape calculations of the  $^{31}\text{P}$  MAS spectra at 4.7 and 9.4 T were done to provide qualitative information about the  $^{31}\text{P}$ – $^2\text{H}$  spin system. The results indicate that residual dipolar effects influence the spectra at both fields. The use of line broadening sufficient to reproduce the experimentally observed line widths also reduces the three individual peaks to a single, broad peak, the maximum of which is less shielded than the isotropic value. Comparison of the apparent isotope shift of the solid with the solution value reported below again indicates (as for phthalimide- $^{15}\text{N}$ , $^2\text{H}$ ) an underestimated value for the solid state. We note that it is generally possible in systems subject to residual dipolar effects for the apparent isotope shift to be either underestimated or overestimated when the individual peaks are not clearly resolved. The sense of the error depends on the signs and relative magnitudes of the pertinent parameters in eqs 3–5.

Isotope effects on  $^{31}\text{P}$  were measured at 9.4 T for a solution-state sample of phenylphosphinic acid in methanol- $d_1$ . The isotope shift was found to be  $^1\Delta(^{31}\text{P}, ^2\text{H}) = -0.407 \pm 0.001$  ppm. Additionally, a primary isotope effect was observed for the P–H spin–spin coupling:  $\Delta_p(^1J(^{31}\text{P}, ^2\text{H})) = -1.4$  Hz. The values for the one-bond  $^{31}\text{P}$ –H couplings are  $^1J(^{31}\text{P}, ^1\text{H}) = 563.6$  Hz and  $^1J(^{31}\text{P}, ^2\text{H}) = 86.3$  Hz. The magnitudes of the long-range  $^{31}\text{P}$ , $^1\text{H}$  spin–spin couplings are  $^3J(^{31}\text{P}, ^1\text{H}) = 14.0$  Hz,  $^4J(^{31}\text{P}, ^1\text{H}) = 3.4$  Hz, and  $^5J(^{31}\text{P}, ^1\text{H}) = 1.7$  Hz. Within the experimental uncertainty (digital resolution) of  $\pm 0.1$  Hz, no secondary isotope effects could be detected for the long-range spin–spin couplings.

**$^1\Delta^{95}\text{Mo}(^{13/12}\text{C})$ : Hexacarbonyl Molybdenum.** As part of a general solid-state NMR study of  $^{95}\text{Mo}$  compounds recently undertaken in this laboratory,<sup>23</sup> the  $^{13/12}\text{C}$ -induced isotope shift of  $^{95}\text{Mo}$  was observed for hexacarbonyl molybdenum,  $\text{Mo}(\text{CO})_6$ . From the  $^{95}\text{Mo}$  MAS spectrum of a powdered sample at 9.4 T, with naturally abundant  $^{13}\text{C}$ ,  $^1\Delta^{95}\text{Mo}(^{13/12}\text{C})$  was found to be  $-0.316$  ppm and  $^1J(^{95}\text{Mo}, ^{13}\text{C}) = 69 \pm 1$  Hz. A solution-state isotope shift of  $-0.316 \pm 0.008$  ppm was measured at 9.4 T for  $\text{Mo}(\text{CO})_6$  in  $\text{CDCl}_3$ . The isotropic chemical shift,  $\delta_{\text{iso}}(^{95}\text{Mo})$ , is  $-1858$  ppm with respect to 2 M  $\text{Na}_2\text{MoO}_4$  in  $\text{D}_2\text{O}$ . The spin–spin coupling  $^1J(^{95}\text{Mo}, ^{13}\text{C}) = 68.4 \pm 0.2$  Hz agrees with the solution-state value of 68 Hz obtained by Mann<sup>24</sup> for  $\text{Mo}(\text{CO})_6$  in  $\text{CHCl}_3$ . All isotope shift values discussed represent the isotopic substitution of a single atom.

**$^1\Delta^{199}\text{Hg}(^{13/12}\text{C})$ : Tetracyanomercure Compounds.** Further examples are provided by  $^{199}\text{Hg}$  spectra of: (i)  $\text{K}_2\text{Hg}(\text{CN})_4$ , natural abundance in  $^{13}\text{C}$ . From an MAS spectrum at 9.4 T, the isotope shift and  $^1J(^{199}\text{Hg}, ^{13}\text{C})$  were determined to be  $+0.27$  ppm and 1512 Hz, respectively. (ii)  $\text{N}(\text{CH}_2\text{CH}_3)_4\text{Na}[\text{Hg}(\text{CN})_4]$ , enriched to 15%  $^{13}\text{C}$  at the cyanide ligands. From an MAS spectrum at 4.7 T, an isotope shift and  $^1J(^{199}\text{Hg}, ^{13}\text{C})$  of  $+0.27 \pm 0.05$  ppm and  $1530 \pm 2$  Hz, respectively, were obtained for those  $^{199}\text{Hg}$  nuclei bonded to one  $^{13}\text{C}$  nucleus. For those  $^{199}\text{Hg}$  nuclei bonded to two  $^{13}\text{C}$  nuclei, the respective values are  $+0.60 \pm 0.05$  ppm and  $1529 \pm 2$  Hz. The isotope effects on the chemical shift of  $^{199}\text{Hg}$  are approximately additive. It was thought that the relatively large  $^{199}\text{Hg}$ – $^{13}\text{C}$  spin–spin coupling of these mercury compounds would make  $\text{N}(\text{CH}_2\text{CH}_3)_4\text{Na}[\text{Hg}(\text{CN})_4]$  a likely candidate to exhibit an isotope effect on  $J_{\text{IS}}$  in

the solid state; however, within the experimental uncertainty, none was observed.

The positive sign of the  $^{199}\text{Hg}$  isotope shift of both  $\text{K}_2\text{Hg}(\text{CN})_4$  and  $\text{N}(\text{CH}_2\text{CH}_3)_4\text{Na}[\text{Hg}(\text{CN})_4]$  represents a deviation from typical observations of the majority of nuclei. However, the only other reported isotope shifts<sup>25</sup> for  $^{199}\text{Hg}$  are positive; the values reported here are comparable to liquid-state values reported<sup>25</sup> for linear, dicoordinated mercury compounds. Because of rapid exchange of the cyanide ligands in solution,<sup>26</sup> it would be difficult, if not impossible, to measure either  $^1\Delta^{199}\text{Hg}(^{13/12}\text{C})$  or  $^1J(^{199}\text{Hg}, ^{13}\text{C})$  for the  $\text{Hg}(\text{CN})_4^{2-}$  ion in solution.

#### 4. Conclusions

Owing partly to the current state of high-resolution solid-state NMR, we have been able to show examples of a wide variety of systems for which it was possible to measure intrinsic isotope effects on the chemical shielding of compounds in the solid state. These solid-state isotope shifts are comparable—with respect to both sign and magnitude—to those measured in solution. These observations are consistent with current theoretical understandings of the origins of isotope effects,<sup>2</sup> which predict that effects for solution and solid systems should be similar provided the pertinent vibrational characteristics are similar in both systems. We hope this report helps to stimulate further interest in exploring isotope effects on chemical shift tensor elements.

Detection of isotope shifts can be difficult at best for spin systems of rigid solids, particularly when  $m'\text{X}$  or  $m''\text{X}$  is a quadrupolar nucleus and residual dipolar effects make it difficult to accurately measure the isotropic chemical shift of the A nucleus. This is in contrast to systems having rotational motions sufficient to produce narrow peaks. Example systems of the latter type are  $\text{NaBH}_4$ ,  $\text{NH}_4\text{Cl}$ , and adamantane, whereas phthalimide and phenylphosphinic acid are examples of the former. The necessity for high-power  $^1\text{H}$  decoupling to remove the dipolar  $^1\text{H}$ –X interactions in the solid state makes it generally impossible to measure isotope effects on spin–spin couplings involving hydrogen atoms. Although not observed in our studies, it should be, in principle, possible to measure such effects for spin pairs involving dilute nuclei, particularly those having narrow peaks and  $J_{\text{IS}}$  of large magnitude.

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