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\( ^1\text{H} \) spin dynamics obtained from off-resonant decoupling in a \(^{13}\text{C}\)-NMR signal

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We extract the exact on-resonance position and local dynamical information of the \(^1\text{H}\) network from a dramatic variation of the peak amplitude of \(^{13}\text{C}\) signals as a function of the carrier frequency of the decoupling field for \(^1\text{H}\). Its Lorentzian dependence is explained within a simple theory.

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The use of different schemes to simplify nuclear magnetic resonance spectra is crucial not only for high resolution in liquids but also in solids. The goal is to effectively eliminate (or minimize) spin–spin couplings. In particular, when acquiring the free induction decay (FID) of a \(^{13}\text{C}\) signal in a solid containing protons, we will be interested in removing the coupling between the \(^{13}\text{C}\) (or \(S\)-spins) and the \(^1\text{H}\) (or \(I\)-spins). In order to do this, one of the usual techniques involves the application of a constant radio frequency (rf) field \(H_1\) at the resonance frequency of the \(I\)-spins during the acquisition.\(^1\) In this way, a narrow highly resolved \(^{13}\text{C}\) signal can be observed at its corresponding chemical shift. On the other hand, the advantage of the cross-polarization technique involves the application of a constant radio frequency (rf) field \(H_1\) at the resonance frequency of the \(I\)-spins during the acquisition.\(^2\) Thus, it is usual in \(^{13}\text{C}\)-NMR measurements in solids containing \(^1\text{H}\) to tune the \(^1\text{H}\)-NMR signal first, and to use that same carrier frequency to perform the decoupling during the \(^{13}\text{C}\) signal acquisition. In this work, we report the effect of a slight off-resonance in the decoupling field with respect to the \(^1\text{H}\) directly bonded to the \(^{13}\text{C}\) in observation, which can deteriorate its signal, constituting a serious drawback if not taken into account. Instead, the same effect can be exploited as a tool for characterization of systems with inhomogeneous coupling networks or clusters with distinguishable spin dynamics.

Although the effect we report here can also be observed in a direct \(^{13}\text{C}\) measurement if a high power decoupling is performed, we discuss it in the framework of a cross-polarization experiment, where the better signal-to-noise ratio allows a more detailed characterization. To understand the effect, let us consider the Hamiltonian describing the evolution of a coupled \(I-S\) system during the acquisition of the \(S\) signal at high resolution conditions, i.e., in the presence of a rotating magnetic field \(H_1\) that interacts with the \(I\)-spins. The interaction of \(H_1\) with the \(S\)-spins is neglected because \(\omega_I\) is set close to the \(I\)-spin resonance, but far from the \(S\)-spin resonance. In the laboratory frame,

\[
\mathcal{H}_L = -\gamma_I \hbar H_0 S_z^0 - \gamma_S \hbar H_0 I_z^0 + 2b_{15} I_z^0 S_z^0 - \gamma_I \hbar H_1 (I_z^0 \cos \omega_I t + I_z^0 \sin \omega_I t) + \mathcal{H}_{11}^L,
\]

where \(\gamma_I\) and \(\gamma_S\) are the gyromagnetic factors of the \(I\)- and \(S\)-spins, respectively, \(H_0\) is the static magnetic field, \(b_{15}\) is the heteronuclear dipolar coupling constant, and \(\mathcal{H}_{11}^L\) accounts for the homonuclear dipolar interaction, truncated with respect to the dominant Zeeman interaction.

After a transformation to a reference frame which is the laboratory one for the \(S\)-spins and one rotating at the carrier frequency \(\omega_I\) for the \(I\)-spins, one gets,

\[
\mathcal{H} = -\hbar \omega_0 I_z^0 - \hbar \omega_0 S_z^0 + 2b_{15} I_z^0 S_z^0 + \mathcal{H}_{11}^L = -\hbar \tilde{\omega} e^{(-i\Omega_1 t)} e^{i\omega_0 t} - \hbar \omega_0 S_z^0 + 2b_{15} I_z^0 S_z^0 + \mathcal{H}_{11}^L,
\]

where \(\Omega_1 = \omega_0 - \omega_I\), with \(\omega_0 = \gamma_I I_z^0\), \(\omega_0 = \gamma_S H_0\) and \(\omega_1 = \gamma_I H_1\), \(\omega = (\Omega_1^2 + \omega_1^2)^{1/2}\) and \(\tan \theta = \Omega_1/\omega_1\). As we are interested in the calculation of the splitting of the \(^{13}\text{C}\) Zeeman levels, we can perform a unitary transformation to find the eigenvalues of

\[
\mathcal{H}^' = \exp(i\Omega_1 t) \mathcal{H} \exp(-i\Omega_1 t) = -\hbar \tilde{\omega} I_z^0 - \hbar \omega_0 S_z^0 + 2b_{15} S_z^0 (I_z^0 \cos \theta + I_z^0 \sin \theta) + \exp(i\Omega_1 t) \mathcal{H}_{11}^L \exp(-i\Omega_1 t).
\]

This is equivalent to taking the quantization axis for the \(I\)-spins along the direction of the effective field, \(\boldsymbol{H}_{\text{eff}}^\perp = 1/\gamma_I (0, \omega_{11}, \Omega_1)\). We neglect, at this stage, the homonuclear interaction and consider the heteronuclear interaction as a perturbation \((\hbar \tilde{\omega} \gg |b_{15}|)\). Then, calculating the correction to the energy levels to first order (i.e., we neglect the term \(S_z^0 I_z^0\)), it is straightforward to see that the effective resonance energy for the \(^{13}\text{C}\) transition is...

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\[ \Delta E = \hbar \omega_{0S} + 2m_I \beta_{IS} \sin \theta = \hbar \omega_{0S} + 2m_I \beta_{IS} \frac{\Omega_I}{\sqrt{\Omega_I^2 + (\omega_{1I})^2}}. \]  

The sign of the second term depends on the spin state of \( I \) \((m_I = \pm \frac{1}{2})\). Then, it is evident that there are two resonance frequencies in the \(^{13}\text{C}\) spectrum whose separation is given by

\[ \delta \nu = \frac{b_{IS}}{\pi \hbar} \frac{\Omega_I}{\sqrt{\Omega_I^2 + (\omega_{1I})^2}}. \]

In a single crystal of ferrocene, we have experimentally observed that, for \( \Omega_I/(2 \pi) \approx 5 \text{ kHz} \) and \( \omega_{1I}/(2 \pi) \approx 70 \text{ kHz} \), there is no resolved splitting in the \(^{13}\text{C}\) spectrum. This tells us that there is some mechanism which collapses the split lines. To produce the collapse of the two lines, the exchange process must be faster than the frequency difference given in (5), i.e., it should have a characteristic time \( \tau \ll 1/\delta \nu \), in which the \(^{13}\text{C}\) resonance frequency is switched between the two possible values. As \( \Delta E \) depends on the spin state of \( I \), we are looking for a process that produces a fluctuation of the \( I \) spins. As has been reported in detail, \(^4\)-\(^9\) the \( I \)-spin state fluctuates due to the dipolar interactions with the other \( I \)-spins. Following the concepts leading to the exchange narrowing theory, \(^1\)-\(^1\) the contribution to the width of the single collapsed line is given by

\[ \Delta \nu_{\text{eff}} = \frac{\pi}{2k} (\delta \nu)^2, \]

where the subscript “off” has been used to emphasize that this contribution to the linewidth is only present under off-resonant decoupling. Here, \( k = 1/\tau \) is the rate of jumps between the states with \( m_I = +1/2 \) and \( m_I = -1/2 \). Thus, the proton directly bonded to the \(^{13}\text{C}\) changes its spin projection with a characteristic time \( \tau \), due to the flip-flop process modulated by the \( I \)-\( I \) dipolar interaction. In addition, there are other contributions to the linewidth \( \Delta \nu^* \), arising from other mechanisms, e.g., the uncertainty principle limit or field inhomogeneities. If the \(^{13}\text{C}\) spectrum has a Lorentzian shape,

\[ S(\nu) = \frac{2A}{\pi} \frac{\Delta \nu}{4(\nu - \nu_0)^2 + \Delta \nu^2}, \]

where \( A \) is the area under the absorption spectrum, the overall linewidth at half height for the \(^{13}\text{C}\) signal is expressed as

\[ \Delta \nu = \Delta \nu_{\text{eff}} + \Delta \nu^* = \frac{\pi \tau}{2} \left( \frac{b_{IS}}{\pi \hbar} \right)^2 \frac{\Omega_I^2}{\Omega_I^2 + \omega_{1I}^2} + \Delta \nu^*. \]

Therefore, the magnitude of the signal maximum or peak amplitude \( S(\nu_0) \) is inversely proportional to its width,

\[ S(\nu_0) = \frac{2A}{\pi} \frac{1}{\Delta \nu}, \]

which is a function of \( \Omega_I \). By defining

\[ \sigma^2 = \frac{4 \Delta \nu^* (\omega_{1I}/2\pi)^2}{\pi \tau^2} \left( \frac{b_{IS}}{\pi \hbar} \right)^2 \approx \frac{4 \Delta \nu^* (\omega_{1I}/2\pi)^2}{\pi \tau^2} \frac{b_{IS}^2}{\pi \hbar} \],

we can rewrite (9) as

\[ S(\nu_0) = \left[ \frac{2A}{\pi \Delta \nu^*} \right] \frac{\sigma^2}{4(\Omega_I/2\pi)^2 + \sigma^2}, \]

where the factor in square brackets is a normalization factor. As in our measurements, \( |\Omega_I| \ll |\omega_{1I}| \) we approximate the last expression by

\[ S(\nu_0) \approx \frac{\sigma^2}{4(\Omega_I/2\pi)^2 + \sigma^2}. \]

The peak amplitude of the \(^{13}\text{C}\) spectrum is a Lorentzian function of \( \Omega_I \) with a width at half height \( \sigma \).

In Fig. 1, we compare the theoretical expression [Eq. (12)] with the experimental results for a single crystal of ferrocene. The good agreement shows that the theoretical model describes the essential process clearly.

It was demonstrated that flip-flop spin motion of abundant spins \( I \) can be varied experimentally over a wide dynamical range, resulting in NMR line broadening and line narrowing effects of rare spins \( S \), dipolar coupled to abundant spins \( I \).\(^4\),\(^5\) In these pioneering works, the effect was explained as arising from the scaling of the \( I \) dipolar Hamiltonian generated by the application of strong rf pulses. In particular, a quenching of the \( I \)-spin flip-flop motion can be achieved by appropriate off-resonant irradiation. However, it should be clear at this stage that the condition \( |\Omega_I| \ll |\omega_{1I}| \) implies that we are changing the angle of the effective field in the rotating frame of the proton resonance with \( H_0 (\hat{\theta}) I \) very slightly. It deviates less than 4° from 90°. Consequently, although the mechanisms producing the effect we are observing are the same as those discussed in these early works, the scaling of the \( I \) dipolar Hamiltonian, given by the factor \((3 \cos^2 \theta I - 1)\), is not the issue here, as it changes only around 1%.

We estimate the value of \( \sigma \) for the particular case of ferrocene, where the width of the \(^1\text{H}\)-NMR spectrum is ap-
proximately 16 kHz, regardless of the orientation of the crystal with respect to the external magnetic field. To do that, it is necessary to determine the value of \( \tau \). While the \( I \)-spins are being irradiated, the dipolar Hamiltonian in the rotating frame, truncated with respect to the interaction with \( H_1 \), is

\[
\mathcal{H}^{II}_1 = -\frac{1}{2} \sum_{j>k} \sum_k d_{jk} \left( 2 I_j^x I_k^x - \frac{1}{2} (I_j^z I_k^z + I_j^y I_k^y) \right).
\]

(13)

Then, the order of magnitude of \( \tau = 2 \pi \hbar / (\langle 1/2 \rangle d_{12}) \), where \( d_{12} \) is the \( I-1 \) nearest neighbors coupling. As usual, we can write \( d_{ij} = 2 \pi \hbar \vec{d}_{ij} \), where \( \vec{d}_{ij} \) is given in Hz, leading to \( \tau = e (2) / d_{12} \) where \( e \leq e_{\text{max}} = 0.63 \) is a fitting parameter that allows us to take into account the exact dynamics of the \( ^1H \) spins. Considering that in ferrocene the cyclopentadienyl rings perform fast rotations around the fivefold symmetry axis averaging the intramolecular interaction parameter,\(^1\) the heteronuclear and homonuclear dipolar couplings are related by \( b_{18} = \alpha d_{12} \) with \( \alpha = 3.699 \). Then, the square of the Lorentzian linewidth is

\[
\sigma^2 = \frac{\Delta \nu (\omega_1/2\pi)^2}{\epsilon \pi d_{12} \alpha^2}.
\]

(14)

Since the contact time \( t_C \) at which the polarization transfer to \(^{13}C \) reaches its maximum is readily measured,\(^13,14\) it is useful to express \( \sigma^2 \) in terms of \( t_C \) instead of \( d_{12} \) by using the relation \( d_{12} = b_{18} / (\alpha 2 \pi \hbar) = 1/(\alpha 2 t_C) \). Thus,

\[
\sigma^2 = \frac{2 t_C \Delta \nu (\omega_1/2\pi)^2}{\epsilon \pi \alpha}.
\]

(15)

In Table I we show the values of \( \sigma_{\exp} \) and \( t_C \) obtained from the experimental data at different orientations of the crystal with respect to the external magnetic field. For comparison we include the values for \( \sigma_{\text{intra}} \) calculated by using \( \epsilon_{\text{intra}} \) and the experimental value of \( \Delta \nu \approx 75 \text{ Hz} \) in Eq. (15).

As can be observed from Table I, the increasing difference between \( \sigma_{\text{intra}} \) and \( \sigma_{\exp} \) at longer \( t_C \) indicates a greater relative importance of the intermolecular contributions to the \(^1H\) dipolar interactions. An interesting application of Eq. (10) consists of the calculation of the homonuclear dynamical time \( \tau \) for the proton(s) directly bonded to the \(^{13}C \). This parameter includes both intramolecular and intermolecular contributions to the homonuclear dipolar interaction. All other parameters in the formula are obtained independently in a simple cross-polarization experiment. In this way, information about the dynamics of the \(^1H \) strongly coupled to the \(^{13}C \) in observation is obtained, including differences in chemical shift which cannot be observed otherwise.

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<th>( t_C (\mu s) )</th>
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<th>52</th>
<th>90</th>
<th>196</th>
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<td>71</td>
<td>69.5</td>
<td>71</td>
<td>72.6</td>
</tr>
<tr>
<td>( \sigma_{\text{intra}} ) (Hz)</td>
<td>2333</td>
<td>2327</td>
<td>2995</td>
<td>4514</td>
<td>5235</td>
</tr>
<tr>
<td>( \sigma_{\exp} ) (Hz)</td>
<td>2806± 80</td>
<td>2860± 73</td>
<td>4446± 116</td>
<td>6913± 360</td>
<td>9804± 900</td>
</tr>
<tr>
<td>( \tau (\mu s) )</td>
<td>320</td>
<td>318</td>
<td>378</td>
<td>774</td>
<td>665</td>
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