Longitudinal Nuclear Relaxation in an A_2 Spin System Initially Polarized through Para-Hydrogen

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Received September 15, 1997

Abstract: $Os_3(CO)_{10}(NCCH_3)_2$ has been hydrogenated with para-hydrogen to yield $H_2Os_3(CO)_{10}$ where the two hydrogen nuclei remain magnetically equivalent and therefore in a singlet state. Despite this equivalence, an enhanced longitudinal magnetization is observed to decrease toward thermal equilibrium. It is postulated that this enhanced magnetization is created through a nuclear relaxation interference mechanism (cross-correlation between dipolar interaction and chemical shift anisotropy); decay curves are then successfully analyzed by means of a spin relaxation theory adapted to this situation.

Introduction

About 10 years ago, proton spin polarization via hydrogenation by para-hydrogen (p-H_2) was discovered.[1,2] This phenomenon comes from a tremendous enhancement of proton NMR transitions in the hydrogenated product provided that hydrogenation originates from p-H_2 through an appropriate catalyzed induced process. This enhancement allows, among other things, one to obtain information about chemical intermediates.[3] This method is quite appealing but is apparently limited to products in which the two hydrogen nuclei become magnetically inequivalent. This can be easily understood by symmetry considerations since p-H_2 corresponds to an unobservable singlet state, highly polarized, which needs to be converted into observable magnetization so as to be detected. Obviously, the easiest way to reach this goal is to transform the relevant state of an A_2 spin system (the so-called longitudinal spin order, represented by the spin function $(1/\sqrt{2})(\alpha\beta - \beta\alpha)$) into states of the same zero quantum number capable of leading to observable transitions (namely the $\alpha\beta$ and $\beta\alpha$ states of an AX spin system). These two states are then highly polarized (or highly populated), leading to intense transitions (for instance, from $\alpha\beta$ to $\beta\beta$), the enhanced intensity arising from the overpopulated $\alpha\beta$ and $\beta\alpha$ energy levels. Thus, it appears that a prerequisite for observing such enhanced NMR spectra is to form hydrogenated products where the two hydrogens become unequivalent. Indeed, whenever the two hydrogens still remain equivalent in the final product, an enhancement was observed only at the ^{13}C satellite level because the presence of a carbon-13 effectively breaks the magnetic equivalence of the two relevant protons.[4] However, in the paper of Haake et al.,[4] it is mentioned that in some instances, an enhanced line is visible at the normal proton resonance, corresponding to ^{12}C-containing molecules. This rather amazing feature is further considered in the present study in which $Os_3(CO)_{10}(NCCH_3)_2$ has been hydrogenated with para-hydrogen to yield $H_2Os_3(CO)_{10}$ where the two protons are seen to remain strictly magnetically equivalent and should not lead to any kind of enhancement. Here, the transfer of the initial p-H_2 polarization to proton longitudinal magnetization will be discussed on the basis of nuclear relaxation processes, and it will be tentatively shown that this is in fact the only means to explain the experimental observations. In brief, as the initial state stems from the longitudinal spin order, an efficient route for ending up with longitudinal magnetization is via a cross-correlation (dipolar-chemical shift anisotropy) term. This relaxation process, known for a long time,[5,6] is now invoked more and more frequently because it turns out to be more effective in experiments carried out with high magnetic fields. The relevant theory (which does not imply a high magnetic field) will be developed with regard to the possible exploitation of experimental data at a molecular level.

Theory

The problem we are dealing with concerns longitudinal relaxation in an A_2 spin $^1/_2$ system, where the only quantity which can be measured is the sum of longitudinal magnetizations of the two nuclei A and A′, i.e.

$$\nu_1 = (1/\sqrt{2})\langle I_z^{A} + I_z^{A'} - 2I_{eq}^{H}\rangle \qquad (1)$$

The factor $(1/\sqrt{2})$ insures normalization of the ν_1 magnetization mode; I_{eq}^{H} stands for the thermal equilibrium magnetization of *one* proton.

In the context of magnetization modes,[7,8] we can substitute the following quantities to the usual modes relevant to a two-

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spin system (which would be $(I_z^{\mathrm{A}} - I_{\mathrm{eq}}^{\mathrm{H}})$, $(I_z^{\mathrm{A}'} - I_{\mathrm{eq}}^{\mathrm{H}})$, $2I_z^{\mathrm{A}}\, I_z^{\mathrm{A}'}$, in addition to the fourth trivial mode, the identity):

$$\nu_1 = (1/\sqrt{2})\langle I_z^{\mathrm{A}} + I_z^{\mathrm{A}'} - 2I_{\mathrm{eq}}^{\mathrm{H}}\rangle$$

$$\nu_2 = \sqrt{2}\langle I_x^{\mathrm{A}}\, I_x^{\mathrm{A}'} + I_y^{\mathrm{A}}\, I_y^{\mathrm{A}'}\rangle = (1/\sqrt{2})\langle I_+^{\mathrm{A}}\, I_-^{\mathrm{A}'} + I_-^{\mathrm{A}}\, I_+^{\mathrm{A}'}\rangle \qquad (2)$$

$$\nu_3 = 2\langle I_z^{\mathrm{A}}\, I_z^{\mathrm{A}'}\rangle$$

ν_1 has been repeated in eq 2 for the sake of completeness. The choice of these magnetization modes stems from the fact that they must commute with the static Hamiltonian H_0. Because A and A′ share the same resonance frequency, the coupling term in H_0 (although not involved in the calculation of line positions and intensities) is of the form $J_{\mathrm{AA}'}\mathbf{I}^{\mathrm{A}}\mathbf{I}^{\mathrm{A}'} = J_{\mathrm{AA}'}(I_x^{\mathrm{A}}\, I_x^{\mathrm{A}'} + I_y^{\mathrm{A}}\, I_y^{\mathrm{A}'} + I_z^{\mathrm{A}}\, I_z^{\mathrm{A}'})$. It may be recalled that no coupling exists between mode ν_1 on the one hand and modes ν_2 and ν_3 on the other hand if cross-correlation is ignored. We shall see that this is not the case here and that the cross-correlation term CSA(A),-dip(AA′) (between the chemical shift anisotropy mechanism at nucleus A or A′ and the dipolar A−A′ interaction) must be accounted for in order to explain transfer from ν_3 (and possibly ν_2) to ν_1. This latter relaxation parameter is often dubbed as “interference term”. A last point concerns the ν_3 mode, also called “longitudinal two-spin order”, and the ν_2 mode: their thermal equilibrium values are zero. However in p-H_2 (as will be seen below), those are the only nonzero quantities with a value several orders of magnitude larger than proton thermal equilibrium magnetization.

We can transform the usual relaxation equations so as to adapt them to the new magnetization modes ν_1, ν_2, and ν_3. This can be written in a matricial form corresponding to a set of three simultaneous first order differential equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix}\nu_1\\ \nu_2\\ \nu_3\end{pmatrix} = \begin{pmatrix}\Gamma\end{pmatrix}\begin{pmatrix}\nu_1\\ \nu_2\\ \nu_3\end{pmatrix} \qquad (3)$$

where the relaxation matrix is symmetrical with the following elements:

$$\Gamma_{11} = -J^{\mathrm{d}}\,(2\omega) - {}^{1}\!/_{4}J^{\mathrm{d}}\,(\omega) - {}^{3}\!/_{2}J^{\mathrm{CSA}}\,(\omega) - 2J^{\mathrm{rf}}\,(\omega)$$

$$\Gamma_{12} = \sqrt{{}^{3}\!/_{2}}J^{\mathrm{CSA,d}}\,(\omega)$$

$$\Gamma_{13} = -\sqrt{3}J^{\mathrm{CSA,d}}\,(\omega)$$

$$\Gamma_{22} = -{}^{1}\!/_{4}J^{\mathrm{d}}\,(\omega) - {}^{3}\!/_{2}J^{\mathrm{CSA}}\,(\omega) - 2J^{\mathrm{rf}}\,(\omega) \qquad (4)$$

$$\Gamma_{23} = 1/(2\sqrt{2})J^{\mathrm{d}}\,(\omega) + 3/\sqrt{2}J^{\mathrm{CSA}}\,(\omega) + 2\sqrt{2}J^{\mathrm{rf}}\,(\omega)$$

$$\Gamma_{33} = -{}^{1}\!/_{2}J^{\mathrm{d}}\,(\omega) - 3J^{\mathrm{CSA}}\,(\omega) - 4J^{\mathrm{rf}}\,(\omega)$$

The J’s are spectral densities whose superscripts indicate the relevant relaxation mechanism (d, dipolar; CSA, chemical shift anisotropy; rf, random fields); $\omega = 2\pi\nu_{\mathrm{H}}$ where ν_{H} is the proton Larmor frequency at the considered magnetic field. In a general way, $J^{rr'}(\omega)$ can be expressed as

$$J^{rr'}(\omega) = K^{rr'}\,\tilde{J}^{rr'}(\omega) \qquad (5)$$

where $\tilde{J}$ is the so-called reduced spectral density whose simplest form is $2\tau_{\mathrm{c}}/(1 + \omega^2\tau_{\mathrm{c}}^2)$, τ_{c} being the relevant correlation time and where

$$K^{\mathrm{d}} = {}^{3}\!/_{5}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma_{\mathrm{H}}^4\hbar^2}{r_{\mathrm{AA}'}^6}$$

$$K^{\mathrm{CSA}} = {}^{2}\!/_{45}(\Delta\sigma)^2(\gamma_{\mathrm{H}}B_0)^2$$

$$K^{\mathrm{CSA,d}} = -{}^{1}\!/_{5}\sqrt{{}^{2}\!/_{3}}\,\frac{\mu_0}{4\pi}\,\frac{1}{2}(3\cos^2\theta - 1)\frac{\Delta\sigma B_0\gamma_{\mathrm{H}}^3\hbar}{r_{\mathrm{AA}'}^3} \qquad (6)$$

In eq 6, the various symbols have their usual meaning (i.e., $\Delta\sigma$, shielding anisotropy; $r_{\mathrm{AA}'}$, distance between the two hydrogen atoms; γ_{H}, proton gyromagnetic ratio, etc.); moreover, in the expression of $K^{\mathrm{CSA,d}}$, θ is the angle between the main axis of the shielding tensor and the internuclear direction so that $K^{\mathrm{CSA,d}}$ may become positive. It can be noticed that $(-\Gamma_{11})$ is the usual relaxation rate of like spins (including the ${}^{3}\!/_{2}$ effect[9]), denoted below by R_1^{A}. Likewise $(-\Gamma_{33})$ represents the specific relaxation rate of the longitudinal spin order and will be denoted by $({}^{2}\!/_{3})R_1^{\mathrm{AA}'}$. With this notation, one has also $\Gamma_{22} = -R_1^{\mathrm{AA}'}/3$ and $\Gamma_{23} = \sqrt{2}R_1^{\mathrm{AA}'}/3$. It is easy to see that, in extreme narrowing conditions ($\omega^2\tau_{\mathrm{c}}^2 \ll 1$), $R_1^{\mathrm{AA}'} = 3R_1^{\mathrm{A}} - ({}^{12}\!/_{5})R_{1,\mathrm{dip}}^{\mathrm{A}}$, where $R_{1,\mathrm{dip}}^{\mathrm{A}}$ is the dipolar contribution to R_1^{A}. We shall further denote $(3/\sqrt{2})J^{\mathrm{CSA,d}}(\omega)$ by $\sigma_{\mathrm{CSA,d}}$. It turns out that ν_2 and ν_3 are not independent but can be gathered into a single normalized mode ν', also orthogonal to ν_1:

$$\nu' = \sqrt{{}^{2}\!/_{3}}(\nu_3 - \nu_2/\sqrt{2}) = \sqrt{{}^{2}\!/_{3}}\langle 3I_x^{\mathrm{A}}\, I_z^{\mathrm{A}'} - \mathbf{I}^{\mathrm{A}}\mathbf{I}^{\mathrm{A}'}\rangle \qquad (7)$$

with the benefit that eqs 3 reduces to two simultaneous first-order differential equations

$$\mathrm{d}\nu_1/\mathrm{d}t = -R_1^{\mathrm{A}}\nu_1 - \sigma_{\mathrm{CSA,d}}\nu'$$

$$\mathrm{d}\nu'/\mathrm{d}t = -\sigma_{\mathrm{CSA,d}}\nu_1 - R_1^{\mathrm{AA}'}\nu' \qquad (8)$$

While the initial value of mode ν_1 is $-\sqrt{2}I_{\mathrm{eq}}^{\mathrm{H}}$, we shall denote by $KI_{\mathrm{eq}}^{\mathrm{H}}$ the initial value of mode ν' (K should be very large and is associated with the initial polarization). As clearly demonstrated in several recent NMR works[10−13] and as p-H_2 corresponds to a singlet state, this can arise solely from a nonzero (initial) value for the longitudinal spin order $(2I_{\mathrm{z}}^{\mathrm{A}}\, I_{\mathrm{z}}^{\mathrm{A}'})$ involved mode ν'. It turns out that if only p-H_2 is considered, the initial state is represented by $\mathbf{I}^{\mathrm{A}}\mathbf{I}^{\mathrm{A}'}$ and $\nu'(0)$ would be zero. Thus, there must exist some step in the hydrogenation process by which $(2I_{\mathrm{z}}^{\mathrm{A}}\, I_{\mathrm{z}}^{\mathrm{A}'})$ is created while the two other product operators $(2I_{\mathrm{x}}^{\mathrm{A}}\, I_{\mathrm{x}}^{\mathrm{A}'})$ and $(2I_{\mathrm{y}}^{\mathrm{A}}\, I_{\mathrm{y}}^{\mathrm{A}'})$ become irrelevant. As suggested below, intermediate products corresponding to an AX spin system can lead to such a situation. However, experimental conditions relatively difficult to control would make useless the evaluation of K and it will be rather considered as a parameter to be determined from experimental data. With these two initial conditions, eqs 8, which are of the Solomon type, can be solved. This yields for the quantity we are interested in (as it is the

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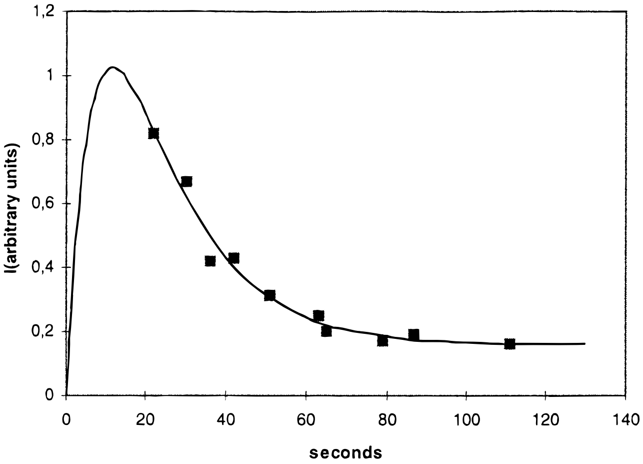

Figure 1. Evolution of the proton magnetization in $H_2Os_3(CO)_{10}$ obtained by hydrogenation of $Os_3(CO)_{10}(NCCH_3)_2$ with para-hydrogen. The 400-MHz data (squares) have been fitted according to eqs 9 and 12. The interest of the theoretical curve (obtained with the parameters resulting from the fit; see text) is to show the essential trend of the relaxation process considered here.

only observable):

$$\begin{gathered} \nu_1(t) = I^{\mathrm{H}}_{\mathrm{eq}}[a_1 \exp(\lambda_1 t) + a_2 \exp(\lambda_2 t)] \\ \lambda_{1,2} = (-R_+ \pm X)/2 \\ a_{1,2} = [-(1/\sqrt{2}) \pm (R_- - \sigma_{\mathrm{CSA,d}} K)/X] \qquad (9) \\ R_\pm = R_1^{\mathrm{A}} \pm R_1^{\mathrm{AA'}} \\ X = (R^2{}_- + 4\sigma^2_{\mathrm{CSA,d}})^{1/2} \end{gathered}$$

Experimental Section

$Os_3(CO)_{10}(NCCH_3)_2$ was prepared according to the procedure published by Nicholls and Vargas.[14] Para-enriched hydrogen was prepared by storing H_2 over Fe_2O_3 at −196 °C for 3−4 h. ^1H NMR spectra were recorded on a JEOL EX-400 and a JEOL EX-90 spectrometers.

The experimental procedure (ALTADENA[15]) was as follows: In a 5-mm screw cap NMR tube, 0.1 mL of a $CDCl_3$ solution containing 0.1 mg of $Os_3(CO)_{10}(NCCH_3)_2$ was mixed with 0.4 mL of a $CDCl_3$ solution saturated with p-H_2. The tube was shaken vigorously and quickly inserted in the spectrometer (the experiment was carried out at 25 °C). The formation of $H_2Os_3(CO)_{10}$ may be easily followed by the change of the solution color from yellow to violet. Spectroscopically, the transformation of $Os_3(CO)_{10}(NCCH_3)_2$ into $H_2Os_3(CO)_{10}$ may be monitored by the appearance of the hydride resonance at −11.5 ppm. Despite being a coordinatively unsaturated species, $H_2Os_3(CO)_{10}$ displays a remarkable chemical stability in the absence of strong donor Lewis bases. In order to deal with a transformation of all $Os_3(CO)_{10}(NCCH_3)_2$ as complete as possible, we have carried out the reaction in large excess of p-H_2 reactant.

The proton NMR signal at 400 MHz was monitored as a function of time, following the end of reaction; its intensity was measured with respect to the signal of 0.00312 mmol of CH_2Cl_2 used as reference. The values given in Figure 1 are therefore in arbitrary units. Although leading to less accurate results, similar experiments were also performed at 90 MHz to check the overall theory.

Results and Discussion

The results presented here arise from p-$H_2Os_3(CO)_{10}$ obtained by hydrogenation with p-H_2 of $Os_3(CO)_{10}(NCCH_3)_2$. This reaction was reported some years ago by Poe and co-workers[16] (see the scheme of Figure 2). The two acetonitrile groups are labile and are replaced by an hydrogen molecule which oxidatively adds to the Os−Os bond to yield two equivalent bridging hydrides. However, one can easily envisage that in such a reaction, the stepwise release of one $NCCH_3$ yields the formation of an intermediate species of formula H(μ-H)$Os_3(CO)_{10}(NCCH_3)$ (Figure 3). In our experimental conditions we cannot detect this intermediate either for its low concentration or for the fact that that the hydrides are exchanging at an intermediate rate at room temperature.[17] As a consequence the A_2 spin system of p-H_2 is transformed into an AX spin system and back to an A_2 spin system in the final compound. This is presumably the mechanism by which the initial state of p-H_2, represented by $\mathbf{I}^{\mathrm{A}}\mathbf{I}^{\mathrm{A'}}$, is converted into a longitudinal two-spin order, $(2I_z^{\mathrm{A}} I_z^{\mathrm{A'}})$, in $H_2Os_3(CO)_{10}$. Thanks to the intermediate step of the AX system symmetry is broken and polarization remains in the form of a state represented by $(2I_z^{\mathrm{A}} I_z^{\mathrm{X}})$ since this occurs in the presence of the static magnetic field. Of course some relaxation may have occurred already at the intermediate step represented by H(μ-H)$Os_3(CO)_{10}(NCCH_3)$ through the various mechanisms described in the theoretical section, and their effect on the populations in the A_2 spin system of the final product may be important. However, in this paper, we show that the overall behavior of the longitudinal magnetization in p-$H_2Os_3(CO)_{10}$ may be well accounted for in terms of a suitable relaxation model based on the occurrence of efficient cross-correlation between dipolar interaction and Chemical Shift Anisotropy.

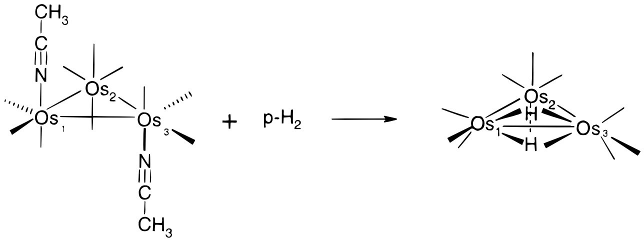

Figure 2. Formation of $H_2Os_3(CO)_{10}$ from $Os_3(CO)_{10}(NCCH_3)_2$.

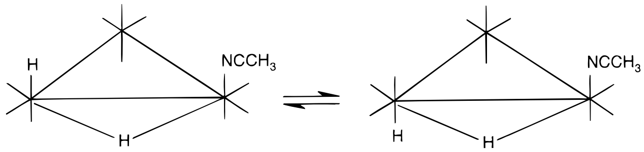

Figure 3. The two exchanging hydrides which occur as intermediates in the hydrogenation of $Os_3(CO)_{10}(NCCH_3)_2$. It can be noted that in these compounds, the two protons are inequivalent.

The general appearance of the evolution of proton magnetization in $H_2Os_3(CO)_{10}$ should be as indicated by the "theoretical" curve of Figure 1 and can be understood as follows: first the

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[17] The NMR characterization of H(μ-H)$Os_3(CO)_{10}(NCCH_3)$ has been possible by reacting $H_2Os_3(CO)_{10}$ with a large excess of $NCCH_3$ (ca. 1:200) in $CDCl_3$. At −40 °C the yellow solution displays, in the hydride region, two pairs of doublets ($J_{\mathrm{HH}} = 3.5$ Hz) for the two isomers reported in Figure 3 (in the relative ratio of 1:4) in addition to the resonance of the unreacted $H_2Os_3(CO)_{10}$ (in the relative ratio of ca. 1:6 with respect to the main product). The main isomer (−10.1 and −17.3 ppm) corresponds to the derivative containing the terminal hydride and the acetonitrile ligands on opposite sides of the Os_3 plane. In the minor isomer (−9.9 and −17.0 ppm) the two ligands are on the same side. As the temperature is increased, a progressive broadening of the hydride resonances takes place accompanied by an increase of the $H_2Os_3(CO)_{10}$ resonance, outlining a shift in the reaction equilibrium. At ambient temperature only the latter signal is detected, and the color of the solution clearly turns to intense violet.

longitudinal spin order polarization (arising from p-H_2 ; mode ν') is converted into longitudinal polarization via the CSA−dipolar interference term; in a second stage, this polarization must necessarily decrease through damping (relaxation) processes toward the thermal equilibrium value. The key parameter is obviously the CSA−dipolar interference term, $\sigma_{\mathrm{CSA,d}}$, which can be expressed, again within the assumptions of extreme narrowing and isotropic reorientation, as a function of $R^{\mathrm{A}}_{1,\mathrm{dip}}$, which is the intramolecular H−H contribution to the relaxation rate

$$\sigma_{\mathrm{CSA,d}} = -\frac{4\pi}{5\sqrt{3}}(3\cos^2\theta - 1)(\nu_0\Delta\sigma)R^{\mathrm{A}}_{1,\mathrm{dip}}\Big/\left(\frac{\mu_0}{4\pi}\frac{\gamma^2\hbar}{r^3}\right) \quad (10)$$

where θ is the angle between the H−H vector and the principal axis of the shielding tensor, $\Delta\sigma$ is the shielding anisotropy, ν_0 is the measurement frequency, and r is the H−H distance. By inserting appropriate numerical values, eq 10 can be written in a more useable form

$$\sigma_{\mathrm{CSA,d}} = -(1.92 \times 10^{-4})(3\cos^2\theta - 1)R^{\mathrm{A}}_{1,\mathrm{dip}}(\Delta\sigma)_{\mathrm{ppm}}(\nu_0)_{10^8\ \mathrm{Hz}}(r^3)_{\mathrm{Å}^3} \quad (11)$$

Quantum chemistry calculations[18] tend to show that the principal shielding axis is perpendicular to the H−H direction while the H−H distance is 2.43 Å. Taking $\Delta\sigma$ as 26 ppm,[19] we obtain $\sigma_{\mathrm{CSA,d}} \approx 0.3\ R^{\mathrm{A}}_{1,\mathrm{dip}}$ at 400 MHz and $\sigma_{\mathrm{CSA,d}} \approx 0.06\ R^{\mathrm{A}}_{1,\mathrm{dip}}$ at 90 MHz.

Experimental data, represented by I(t), have tentatively been exploited according to eqs 9 recast as

$$I(t) = I^{\mathrm{H}}_{\mathrm{eq}}[2 + \sqrt{2}a_1\exp(\lambda_1 t) + \sqrt{2}a_2\exp(\lambda_2 t)] \quad (12)$$

If the whole evolution was available, all unknowns implied in eqs 9 (i.e., $I^{\mathrm{H}}_{\mathrm{eq}}$, K, R^{A}_1, $R^{\mathrm{A,A'}}_1$, or alternatively $R^{\mathrm{A}}_{1,\mathrm{dip}}$, and $\sigma_{\mathrm{CSA,d}}$) could be derived. Unfortunately the experimental conditions preclude the detection of the first part of the evolution curve and the available data points have been found to be sensitive only to $I^{\mathrm{H}}_{\mathrm{eq}}$ (obtained with the arbitrary units used for I(t)), R^{A}_1, $R^{\mathrm{A}}_{1,\mathrm{dip}}$ (as long as the constraint of being smaller than R^{A}_1 is imposed), and to the product $K\sigma_{\mathrm{CSA,d}}$. As a consequence, we were unable to determine unambiguously $\sigma_{\mathrm{CSA,d}}$, and we thus relied on the above approximate relationships between $\sigma_{\mathrm{CSA,d}}$ and $R^{\mathrm{A}}_{1,\mathrm{dip}}$. The following values were obtained at 400 MHz: $K = -286$, $\sigma_{\mathrm{CSA,d}} = 0.0075\ \mathrm{s}^{-1}$, $R^{\mathrm{A}}_1 = 0.0625\ \mathrm{s}^{-1}$, and $R^{\mathrm{A}}_{1,\mathrm{dip}} = 0.025\ \mathrm{s}^{-1}$. Experimental data are seen to be in agreement with the present theory (see Figure 1). Moreover, the parameters so obtained appear reasonable and consistent (as expected K, which can be recalled to reflect the initial polarization, is found to be negative while $\sigma_{\mathrm{CSA,d}}$ is found to be positive). This consistency has been further checked with the 90 MHz data; however, due to less reliability of these data, this was done without fitting but in verifying visually that the following set of parameters agrees with the experimental results (in particular, we chose a $\sigma_{\mathrm{CSA,d}}$ value about four times smaller than the one found at 400 MHz): $K = -2000$, $\sigma_{\mathrm{CSA,d}} = 0.0002\ \mathrm{s}^{-1}$, $R^{\mathrm{A}}_1 = 0.06\ \mathrm{s}^{-1}$, and $R^{\mathrm{A}}_{1,\mathrm{dip}} = 0.035\ \mathrm{s}^{-1}$. It can be observed that similar values are obtained for $R^{\mathrm{A}}_{1,\mathrm{dip}}$ which yields a correlation time of 6−8 ps. At least the order of magnitude seems correct owing to the underlying assumptions: isotropic reorientation and a H−H distance equal to 2.43 Å.

This study indicates that nuclear spin polarization arising from para-hydrogen can be converted into longitudinal magnetization by a relaxation process. By contrast with recent experiments dealing with dipolar cross-relaxation as a means of transfer from laser-polarized xenon,[20] we invoke here a process based on cross-correlation between two different relaxation mechanisms: dipolar interaction and chemical shift anisotropy. It can be further noted that this interference mechanism has been until now neglected in relaxation studies of hydride ligands in spite of the fact that many investigations on hydride derivatives have been carried out at high magnetic fields.

JA973240W

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