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Electron Spin Polarization Transfer to *ortho*-H$_2$ by Interaction of *para*-H$_2$ with Paramagnetic Species: A Key to a Novel para → ortho Conversion Mechanism

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ⓢ *Supporting Information*

ABSTRACT: We report that at ambient temperature and with 100% enriched *para*-hydrogen (p-H$_2$) dissolved in organic solvents, paramagnetic spin catalysis of para → ortho hydrogen conversion is accompanied at the onset by a negative *ortho*-hydrogen (o-H$_2$) proton NMR signal. This novel finding indicates an electron spin polarization transfer, and we show here that this can only occur if the H$_2$ molecule is dissociated upon its transient adsorption by the paramagnetic catalyst. Following desorption, o-H$_2$ is created until the thermodynamic equilibrium is reached. A simple theory confirms that in the presence of a static magnetic field, the hyperfine coupling between unpaired electrons and nuclear spins is responsible for the observed polarization transfer. Owing to the negative electron gyromagnetic ratio, this explains the experimental results and ascertains an as yet unexplored mechanism for para → ortho conversion. Finally, we show that the recovery of o-H$_2$ magnetization toward equilibrium can be simply modeled, leading to the para → ortho conversion rate.
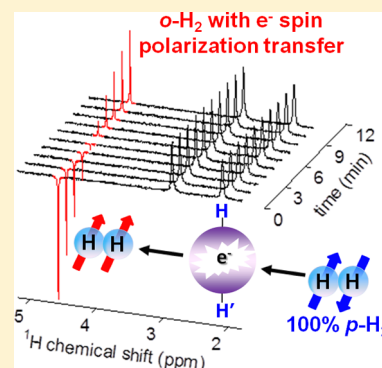
The concept of paramagnetic spin catalysis of para → ortho conversion in molecular H$_2$, although introduced several decades ago,[1] has been a long-standing subject of research concerning, in particular, the underlying mechanisms. As a matter of fact, recent studies[2−4] witness that it is still a topical matter.

The dihydrogen molecule can exist in two different spin states: the ortho-hydrogen (o-H$_2$) spin isomer, often represented by the two nuclear spins in a parallel configuration (in fact, in a triplet state), and the para-hydrogen (p-H$_2$) spin isomer, often represented by the two nuclear spins in an antiparallel configuration (in fact, in a singlet state). At room temperature, the equilibrium proportions of o-H$_2$ and p-H$_2$ are, respectively, 0.75 and 0.25.[1,5] By means of appropriate devices, it is possible to reach a 50% enrichment in p-H$_2$ at liquid nitrogen temperature (77 K) or even a 100% enrichment at 20 K.[5,6] When the sample is brought back to room temperature, recovery to equilibrium can be very slow: up to weeks or even months in the gaseous state or days when p-H$_2$ is dissolved in dry organic solvents.[1,5] In both cases, it has been recognized that the presence of paramagnetic species accelerates the recovery to equilibrium, that is, the para → ortho conversion.[5,7] As early as in 1933, Wigner proposed a theory[8] by which collisions and a magnetic field gradient across the H$_2$ molecule can account for this conversion.

We shall be concerned here with solution state and we shall distinguish between two different situations. In the first situation, the H$_2$ molecule is not chemically bound (neither covalently nor by hydrogen bonds) to the paramagnetic species. In that case, as shown recently,[9] the Wigner theory applies. Conversely, in the second situation, which is the subject of the present study, there is a definite contact between the H$_2$ molecule and the paramagnetic complex or ion, which therefore acts as a true catalyst. Some discrepancies were noticed with respect to the Wigner theory, in particular concerning the distance between the hydrogen atoms and the unpaired electron(s),[10,11] and several theoretical works have been published, proposing new mechanisms for the para → ortho conversion.[12−14]

In the course of a ^{1}H NMR study dealing with 100% enriched p-H$_2$, dissolved in organic solvents at room temperature and in the earth magnetic field (see Supporting Information (SI) for details), we came across a rather puzzling effect that has never been described in the literature (to the best of our knowledge). When a paramagnetic species (such as Cr(acac)$_3$) is added to a deuterated organic solvent (such as acetone-d_6), we observe that upon insertion of the sample in the magnetic field of the NMR spectrometer, the o-H$_2$ NMR signal appears immediately but as a *negative* peak (Figure 1). We shall quantitatively explain later why such behavior could
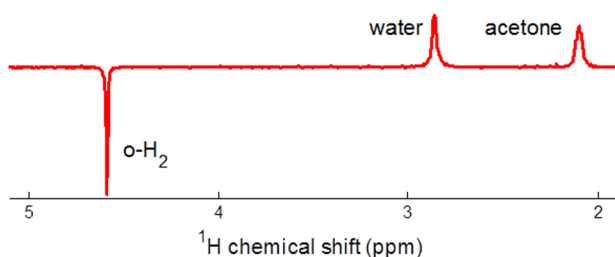
Figure 1. ^{1}H NMR spectrum of o-H$_2$ (negative signal at 4.6 ppm) in a 25 mM solution of Cr(acac)$_3$ in acetone-d_6 (~0.38 mL; residual protons showing up at 2.0 ppm). The spectrum has been recorded at 200 MHz within 30 s after sample insertion in the magnet and within 1 min after insertion of 100% enriched p-H$_2$ at 5 bar into a gastight 5 mm NMR tube (including ~3 s shaking time in earth magnetic field). The peak at 2.9 ppm is that of residual water (~0.02 ± 0.01 mmol/L) in the acetone-d_6 used in this work.

not be observed in previous works.[2,10,15] Basically, this is because 50% enriched p-H$_2$ was used, with the initial non-null proportion of o-H$_2$ masking this negative peak.

Clearly, the only way to explain the initially negative o-H$_2$ signal is an electron polarization transfer because the electron gyromagnetic ratio, γ_e, is negative (while the proton gyromagnetic ratio, γ_H, is positive). Hence, this implies that (i) o-H$_2$ is created and (ii) some interaction, capable of inducing this transfer, exists.

We find that the phenomenon here described occurs for paramagnetic entities other than Cr(acac)$_3$, such as CuSO$_4$·5H$_2$O and even residual O$_2$ resulting from an incomplete degassing of the solution prior to p-H$_2$ introduction. (See Figures S1 and S2 in the SI, respectively). All of these species behave as a catalyst (denoted by C in the following) and thus are able to adsorb a p-H$_2$ molecule according to the following reaction

$$C + p\text{-}H_2 \rightarrow CHH' \tag{1}$$

For most catalysts, the identity of the H$_2$ molecule is lost and the two hydrogen atoms become distinct;[16,17] however, upon desorption, H$_2$ molecules are necessarily reconstituted. The question is then to know which spin isomers are formed. The answer rests naturally on thermodynamic considerations: o-H$_2$ is preferentially formed until the thermodynamic proportions are reached. Therefore, because eq 1 is the direct reaction involved in a chemical equilibrium, the inverse reaction should be written

$$CHH' \rightarrow C + o\text{-}H_2 \tag{2}$$

Along the same thermodynamics lines, whenever o-H$_2$ is adsorbed by the catalyst, o-H$_2$ is formed again if equilibrium is not attained. Of course, under thermal equilibrium conditions, the adsorption−desorption process continues and, upon desorption, o-H$_2$ and p-H$_2$ are formed according to their respective statistical proportions (75 and 25%). Although the other mechanisms of para → ortho conversion[2] are superimposed to the previously described process, the latter is expected to be active (as confirmed by the observation of a negative o-H$_2$ peak with 100% enriched p-H$_2$ for all the systems investigated here), provided that (i) there is a definite contact between the H$_2$ molecules and the paramagnetic catalyst and that (ii) their concentration is not negligibly small. We noted a different behavior for Wilkinson's[18] and Crabtree's[19] catalysts. For those catalysts, the whole H$_2$ molecule substitutes for a

ligand and, consequently, does not participate in the above described mechanism. As a matter of fact, it is well known that these types of catalysts must be used for the PHIP (para-induced-hydrogen hyper-polarization) hydrogenation reactions by a pairwise transfer of both atoms of the hydrogen molecule to the substrate molecule.[5] Indeed, we did not observe a negative o-H$_2$ signal with [Rh(NBD)dppb]$^+$[BF$_4$]$^-$, which is a catalyst commonly used for hydrogenation reactions and which is paramagnetic as well.[20] This is in agreement with the recent observation of hyperpolarized absorptive o-H$_2$ signal in solutions containing Crabtree's catalyst (with 100% p-H$_2$).[21]

While the mechanism for para → ortho conversion discussed here (to date not reported) is revealed by electron polarization transfer, the latter has yet to be elucidated. Since our experimental observations concern the liquid phase, the only electron−proton interaction on which we can rely is the so-called hyperfine coupling, already envisaged for the para → ortho conversion at gas/solid interfaces.[12] We present here density-operator-based calculations that actually demonstrate the feasibility of such polarization transfer. When H and H′ come into contact with the paramagnetic complex, their wave function remains that of the singlet state which, by nature, has no spin. Therefore, at the beginning of the adsorption stage, H and H′ are not subjected to any nuclear Zeeman interaction. Since electron spin relaxation is very fast with respect to proton spin relaxation, the electron Zeeman interaction can also be disregarded, as far as the evolution of proton spins is concerned. To simplify the forthcoming calculations, we shall proceed with a single electron spin and a single proton.

From the previous considerations, we can assume that this system is exclusively governed by the hyperfine Hamiltonian (i.e., by the scalar interaction between the electron spin and the nuclear spin)

$$\hat{H}_{\text{hyperfine}} = A(\hat{I}_x\hat{S}_x + \hat{I}_y\hat{S}_y + \hat{I}_z\hat{S}_z) \tag{3}$$

where A is the hyperfine coupling, while $\hat{I}$ and $\hat{S}$ represent nuclear and electron spin operators, respectively.[22]

Our goal is now to determine the longitudinal magnetization of o-H$_2$ at the end of reaction 2. This amounts to derive an evolution equation for I_z. The general method, described in detail elsewhere,[23] is to use the density operator formalism and the Liouville−von Neumann equation. This leads to

$$\frac{dI_z}{dt} = -\frac{A}{2}(2I_xS_y - 2I_yS_x) \tag{4}$$

and by applying the same procedure[23] to the quantity corresponding to zero-quantum coherences that appears in the right-hand side of eq 4, we obtain

$$\frac{d}{dt}(2I_xS_y - 2I_yS_x) = A(I_z - S_z) \tag{5}$$

Now, it will be assumed (quite reasonably) that, because $\gamma_e \approx -658\gamma_H$, the populations of electron spin energy levels are not affected by the hyperfine coupling between proton and electron so that S_z can be substituted by $S_{\text{eq}} = -658I_{\text{eq}}$.

We thus arrive at the evolution equation of I_z

$$\frac{d^2}{dt^2}(I_z - S_{\text{eq}}) + \frac{A^2}{2}(I_z - S_{\text{eq}}) = 0 \tag{6}$$

With the initial conditions $I_z(0) = 0$ and $2I_xS_y(0) - 2I_yS_x(0) = 0$, eq 6 is readily solved

$$I_z = S_{eq}\left(1 - \cos\frac{A}{\sqrt{2}}\tau\right) \qquad (7)$$

where τ is the time during which the two protons originating from p-H_2 are in contact with the paramagnetic species. Evidently, because of the minus sign of γ_e, the sign of the initial o-H_2 signal will be that of S_{eq}, which is negative. In summary, eq 7 tells us that the negative amplitude of the proton signal at the onset of the para → ortho conversion in liquid phase is a definite indication of the interaction between the dissociated H_2 molecule and the paramagnetic species present in the solution.

For the sake of completeness, we demonstrate now that the electron spin polarization transfer by interaction with a paramagnetic species arises exclusively from p-H_2 and not from o-H_2. o-H_2 possesses a nonzero spin and is therefore subjected, in addition to $\hat{H}_{hyperfine}$, to the nuclear Zeeman interaction, $\hat{H}_{Zeeman} = -\nu_H \hat{I}_z$, where ν_H is the ^1H Larmor frequency. Equation 4 is unchanged but eq 5 becomes

$$\frac{d}{dt}(2I_xS_y - 2I_yS_x) = \nu_H(2I_xS_x + 2I_yS_y) + A(I_z - S_{eq}) \qquad (8)$$

As $\upsilon_H \gg A$ at magnetic fields of the current NMR spectrometers, the last term in the right-hand-side of eq 8 is negligible, thus precluding any possibility of polarization transfer from the electron spin system. It can be noticed that this statement is equivalent to retaining only the term $A\hat{I}_z\hat{S}_z$ in the hyperfine Hamiltonian (as is commonly done for the J-coupling Hamiltonian when analyzing first-order NMR spectra).

The next (and final) step will consist in explaining and analyzing the observed o-H_2 signal buildup as a function of the time elapsed from the introduction of 100% enriched p-H_2 into the NMR tube. This is simply performed by successive radio frequency 90° pulses, each followed by signal acquisition (see experimental details in SI) and Fourier transform. It can be noted that these observing pulses do not actually perturb the o-H_2 buildup because the o-H_2 magnetization recovers in a time of ca. five times the normal relaxation time of o-H_2 (R_1^{-1} on the order of some seconds as compared with the buildup time scale, which is larger by two to three orders of magnitude; see our data in Table 1). The amplitude of the NMR peak thus reflects the o-H_2 magnetization evolution (it can be recalled that p-H_2 is NMR silent). A typical example is shown in Figure 2.

When the paramagnetic concentration largely exceeds that of H_2 in the solution, the overall para → ortho conversion rate is expected to be dominated by the paramagnetic-induced contribution, denoted here as r_{po}. In this case, the evolution
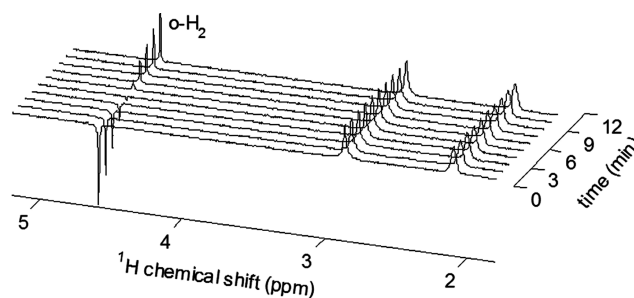

Figure 2. Typical time evolution of the o-H_2 peak, initially *negative* as shown in Figure 1. Time zero corresponds to the insertion of the sample in the NMR spectrometer magnet, ca. 1 min after dissolution of 100% enriched p-H_2 in the solvent containing paramagnetic species.

equation for the normalized o-H_2 population N^{ortho} ($N^{ortho} + N^{para} = 1$) can be written

$$\frac{dN^{ortho}}{dt} = -r_{po}(N^{ortho} - 0.75) = r_{po}(N^{para} - 0.25) \qquad (9)$$

where the condition $dN^{ortho}/dt = -dN^{para}/dt$ reflects the irreversibility of the para → ortho conversion process. As p is the initial para-enrichment ($0.25 < p < 1$), eq 10 has for solution

$$N^{ortho}(t) = 0.75\left(1 - \left(\frac{p - 0.25}{0.75}\right)e^{-r_{po}t}\right) \qquad (10)$$

Because of the negative electron polarization transfer, the proton magnetization measured before having reached the equilibrium para/ortho ratio is not simply proportional to the respective amount of o-H_2. Therefore, we have to make a connection between the measured o-H_2 magnetization and $N^{ortho}(t)$ and, for that purpose, to cope with o-H_2 specific relaxation. First, it can be recognized that the nuclear spins of o-H_2 get polarized in the magnetic field subsequently to the creation of o-H_2 molecules. This leads to nuclear magnetization in a short time (again related to the o-H_2 longitudinal relaxation time) as compared with the total time for reaching the global equilibrium magnetization. Hence, it could be assumed from eq 10 that the evolution of nuclear magnetization is proportional to $N^{ortho}(t)$. However, as previously emphasized, one has to subtract from such magnetization the contribution resulting from electron polarization transfer at time t. This contribution, assuming that it survives for a time ΔT (still related to the o-H_2 longitudinal relaxation time), is proportional to $(dN^{ortho}/dt)\Delta T = (p - 0.25)r_{po}e^{-r_{po}t}\Delta T$. The quantity to be subtracted is therefore of the form $((p - 0.25)/0.75)Ke^{-r_{po}t}$, where the positive constant K includes, inter alia, the strength and efficiency of the hyperfine coupling (see eq 7). Thus, in a general way, the measured magnetization can be expressed as

$$M_z(t) = M_0\left(1 - \left(\frac{p - 0.25}{0.75}\right)s \cdot e^{-r_{po}t}\right) \qquad (11)$$

with $s = ((M_0 + K)/M_0) \geq 1$. We note that eq 11 is consistent with the initial and equilibrium conditions: $M_z(0) = -K$ (if $p = 1$) and $M_z(\infty) = M_0$. The experimental para → ortho recovery buildup can be fitted against eq 11 in the same way as longitudinal NMR relaxation data, however without the restriction $s \leq 2$. The important point that appears in eq 11 is that the rate of para → ortho conversion can be easily deduced from the experimental data, along with the parameter

Table 1. At 100% para-Enrichment: Estimates of the Parameters r_{po}, R_{po} and s governing the o-H_2 Signal Recovery in Acetone-d_6 at Increasing Concentration [C] of Cr(acac)$_3$ Catalyst[a]

[C] (mM)	r_{po} (h^{-1})	R_{po} (h^{-1})	s	R_1 (s^{-1})
0		0.06 ± 0.01	0.99 ± 0.01	0.46 ± 0.03
2.5 ± 0.2	0.4 ± 0.1	1.1 ± 0.1	1.6 ± 0.3	0.67 ± 0.04
4.0 ± 0.1	0.9 ± 0.1	2.4 ± 0.3	1.8 ± 0.3	0.74 ± 0.04
25 ± 1	8 ± 1		1.97 ± 0.03	2.1 ± 0.1
90 ± 1	17 ± 3		1.8 ± 0.1	4.0 ± 0.2

[a]Corresponding classical R_1 values of o-H_2 are also reported.

s, which is mostly associated with the existence of a hyperfine interaction. A typical example of single-exponential buildup with 100% enriched p-H_2 is shown in Figure 3 (left) for a 25 mM solution of Cr(acac)$_3$ in acetone-d_6 (see also the data in Table 1).
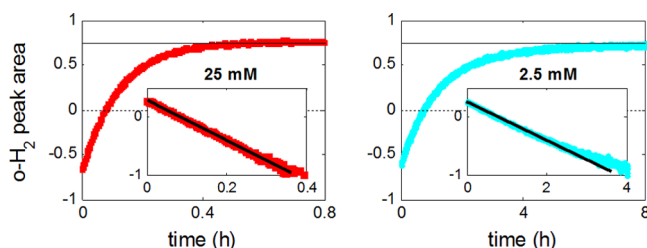

Figure 3. At 100% para-enrichment: Buildup of the normalized o-H_2 signal amplitude in an acetone-d_6 solution containing Cr(acac)$_3$ at 25 (left, up to 0.8h) and 2.5 mM (right, up to 8h) showing single- and biexponential behavior, respectively. The inset in each plot is a semilogarithmic representation. (The guide-to-the-eye solid line corresponds to a single-exponential decay.)

We note that with $p = 0.5$ and s on the order of 2 or less (at least with the systems investigated here), the initial signal $M_z(0)$ is seen to be positive, in agreement with our experimental findings obtained at 50% para-enrichment on the present systems (see Figure S3 in SI) and with the results given in the literature.[2,15]

At relatively low paramagnetic concentration, it may happen that the para → ortho conversion due to other mechanisms competes with that due to adsorption−desorption of p-H_2 (assumed until now to be overwhelming). In this case, eq 11 has to be modified as follows

$$M_z(t) = M_0\left\{1 - \left(\frac{p - 0.25}{0.75}\right)\left[e^{-R_{po}t} + (s - 1)e^{-r_{po}t}\right]\right\}$$

(12)

Here R_{po} is the sum of r_{po} and of conversion rates due to other mechanisms. Experimental data can then be fitted according to eq 12 with R_{po}, r_{po}, and s as unknowns. A typical example of biexponential recovery is shown in Figure 3 (right) for a 2.5 mM solution of Cr(acac)$_3$ in acetone-d_6. The fitting parameters deduced from the different concentrations of Cr(acac)$_3$ investigated in this work are gathered in Table 1.

As expected, the para → ortho conversion rate due to the adsorption−desorption process (r_{po}) is seen to increase with the paramagnetic species concentration. As soon as this concentration becomes significant, this mechanism largely overcomes the other ones (R_{po} in the first row of Table 1).

In conclusion, it can be stated that the electron polarization transfer to o-H_2 molecules has unraveled a new mechanism for the conversion of p-H_2 to o-H_2 dissolved, at room temperature, in organic solvents containing paramagnetic species. This mechanism stems from the dissociation of the hydrogen molecule when it comes in contact (by transient adsorption) with proper paramagnetic species (without pairwise interaction). As these systems behave as catalysts, a new H_2 molecule is formed upon desorption. It is o-H_2 if the populations corresponding to thermal equilibrium are not yet reached.

At large paramagnetic concentration, this mechanism is relatively fast as compared with the other possible mechanisms responsible for the para → ortho conversion and does not

require any static magnetic field; however, when the buildup of o-H_2 is monitored by NMR, unpaired electrons become necessarily polarized and, as a side effect, this polarization can be transferred to the o-H_2 nuclear spins. The major interest of this purely spectroscopic feature is that it provides not only a definite proof of the mechanisms of para → ortho conversion but also directly the para → ortho conversion rate related to the adsorption−desorption mechanism.

■ **ASSOCIATED CONTENT**

Ⓢ Supporting Information

Sample preparation and experimental details of p-H_2 production and ^1H NMR experiments; initially negative o-H_2 peak in solutions containing paramagnetic species other than Cr(acac)$_3$ (CuSO$_4$·5H$_2$O or even residual O$_2$) with dissolved 100% p-H_2; and results of the experiments done with 50% para-enrichment (in Cr(acac)$_3$ solutions). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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