Mechanism of nuclear spin initiated *para*-H_2 to *ortho*-H_2 conversion

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In this paper a quantitative explanation for a diamagnetic *ortho*/*para* H_2 conversion is given. The description is based on the quantum-mechanical density matrix formalism originally developed by Alexander and Binsch for studies of exchange processes in NMR spectra. Only the nuclear spin system is treated quantum-mechanically. Employing the model of a three spin system, the reactions of the hydrogen gas with the catalysts are treated as a phenomenological rate process, described by a rate constant. Numerical calculations reveal that for nearly all possible geometrical arrangements of the three spin system an efficient spin conversion is obtained. Only in the chemically improbable case of a linear group H–X–H no spin conversion is obtained. The efficiency of the spin conversion depends strongly on the lifetime of the H–X–H complex and on the presence of exchange interactions between the two hydrogens. Even moderate exchange couplings cause a quench of the spin conversion. Thus a sufficiently strong binding of the dihydrogen to the *S* spin is necessary to render the quenching by the exchange interaction ineffective.

Introduction

ortho-Hydrogen and *para*-hydrogen are two species of molecular dihydrogen.[1] They are distinguished by different sets of nuclear (spin and rotational) states. *para*-H_2 exhibits a pure nuclear singlet state and is associated *via* the Pauli exclusion principle with rotational states with even spatial symmetry. *ortho*-H_2 exhibits a nuclear triplet state and is associated with rotational states with odd spatial symmetry. Both dihydrogen states are stable as a gas and in liquid solutions.[2] In thermal equilibrium at room temperature each of the three *ortho*-states and the single *para*-state has practically equal probability. By contrast, at temperatures below liquid nitrogen mainly the energetically lower *para*-state is populated. Without external catalysts the interconversion between the *para*- and *ortho*-state is very slow and consequently *para*- and *ortho*-H_2 can be stored for several months. The mechanisms of the *ortho*/*para* conversion of hydrogen have been the topic of various experimental and theoretical studies. This interest in the conversion was triggered by three main reasons, namely (i) the application of combined studies of the *ortho*/*para* spin conversion of dihydrogen and of the hydrogen/deuterium scrambling reactions as tools for the elucidation of the mechanisms of catalytic hydrogenation reactions;[3,4] (ii) the application of *para*-hydrogen as an agent for the sensitivity enhancement of liquid state NMR,[5–7] in particular for studies of catalysis; and (iii) the quantum mechanical nature of the *ortho*- and *para*-states, which is interesting by itself; (iv) the usage of *ortho*/*para*-water ratios as remote sensors for the thermal history of the ice core of comets;[8–11] (v) to understand the mechanisms of the conversion of *para*-formaldehyde to *ortho*-formaldehyde by surface adsorption.[12]

The studies of dihydrogen metal complexes started when Wilkinson found the first catalysts which are able to take up and easily activate molecular dihydrogen during the hydrogenation of double bonds.[13] Later Bowers and Weitekamp suggested to use *para*-hydrogen as a diagnostic tool in hydrogenation reactions,[14,15] suggesting the so-called PASADENA (parahydrogen and synthesis allow dramatically enhanced nuclear alignment) and ALTADENA (adiabatic longitudinal transport after dissociation engenders net alignment) experiments. These types of experiments are nowadays mainly referred to under the common, more general, acronym PHIP (parahydrogen induced polarization).[16] The transformation of the molecular rotational order into nuclear spin order during the hydrogenation reaction leads to typical polarization patterns in the NMR spectra of the hydrogenation products. In the PASADENA experiment the reaction is carried out in the presence of a magnetic field, and in the ALTADENA experiment the reaction is carried out in the absence of a magnetic field and the sample is then adiabatically introduced into the NMR spectrometer. Both experiments lead to different polarization patterns, which are visible in the resulting NMR spectra.

Following the original proposal of Weitekamp and Bowers, *para*-H_2 was successfully employed for various NMR studies of catalytic reactions in one-[17–19] and two-dimensional NMR spectroscopy.[20] These techniques are an important diagnostic tool for mechanistic studies of chemical reactions[17,18,21–38] It was even suggested to employ the pure singlet quantum state of *para*-H_2 as an initial state for NMR quantum computing.[39] Triggered by the importance for catalytic studies the spin

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dynamics of *para*- and *ortho*-H_2 was carefully studied[40] employing a density matrix formulation of the NMR line shape theory, which is based on the original NMR line shape theory of exchanging protons, developed by Alexander[41] and Binsch.[42]

As already mentioned above, the *ortho*/*para*-conversion is a slow process, which needs the aid of some catalyst. In the literature three different mechanisms for the *ortho*/*para*-conversion have been discussed, namely a paramagnetic mechanism where the spin conversion is caused by the magnetic interaction of the hydrogen spins with paramagnetic centers, for example, unpaired electron spins; a pressure dependent mechanism, where the spin conversion is catalyzed by high pressure in solid hydrogen, and a chemical exchange mechanism where the spin conversion is achieved by a chemical hydrogen exchange reaction.

The original theory of the conversion was established by Wigner already in 1933.[43] The essence of his theory is that a magnetic moment located at the catalytic center X is scattered by a hydrogen molecule whose center sits for a while close to the center X. This causes a non-zero magnetic dipolar interaction between the magnetic moment of the catalytic center and the two molecular nuclear spins, which leads to the Wigner rate of spin conversion. Paramagnetic impurities, *i.e.* unpaired electron spins or electrons with orbital momentum were identified as catalytic centers. Examples of paramagnetic catalysts for the *ortho*/*para*-conversion are hydrogen atoms in solid hydrogen[44] or copper atoms on copper surfaces.[45] Later, the theory of Wigner was revised by Milenko and Sibileva,[46] who included the molecular velocity of the hydrogen molecules to have a better description of the temperature dependence of the conversion process. Recently, the *ortho*/*para*-hydrogen spin conversion was used as a prototype for nuclear spin conversions in other molecules.[47]

In a recent publication[48] some of us have reported experimental evidence for an efficient *ortho*/*para*-H_2 spin conversion in a purely diamagnetic compound where practically no paramagnetic impurities are present. In this publication we suggested that the spin conversion was the result of nuclear spin interactions between the hydrogen spins of the *para*-H_2 and nuclear spins and we proposed the existence of a new, nuclear spin mechanism of the *ortho*/*para*-H_2 spin conversion, which exists in parallel to the other mechanisms. A similar conversion process, observed by Vaska *et al.*[49] for certain catalytic reactions, was attributed to a metathesis in a tetrahydride intermediate.

In a set of papers[50–54] some of us have proposed and studied a general model of coherent and incoherent dihydrogen exchange effects in the coordination sphere of transition metals. This theory is now adapted to study the conversion process and we give a quantitative analysis of this conversion channel and present a density matrix theory of the spin conversion which explains the observed spin conversion, using the simple model of a three spin system in zero magnetic field.

This model is schematically pictured in Fig. 1. The left side shows the three states of the conversion process. We assume that there is a large reservoir of *para*-H_2 which is in contact with the purely diamagnetic catalyst X. In the free dihydrogen state, the rotational energy causes a large energy gap between the lowest *para*- and *ortho*-state. In the initial state all hydrogen molecules are prepared in the *para*-state, *i.e.* in the nuclear singlet state, for example by suitable cooling of the system.

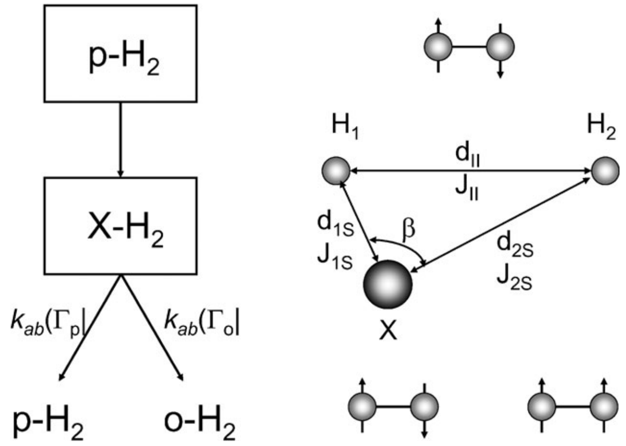

Fig. 1 Schematic model of the *ortho*/*para*-H_2 conversion on solid surfaces. Left: starting from the initial *para*-H_2 state a complex of the type X–H_2 is formed. In this complex the spin conversion of the hydrogen occurs. During the decay of the X–H_2 complex the projections on the *para*- and *ortho*-subspaces are formed, *i.e.* free *para*-H_2 and *ortho*-H_2 is formed. Right: schematic view of the different dihydrogen configurations and their spin states: Top: initially the two hydrogens are in the *para*-state, symbolized by antiparallel nuclear spins and short H–H distance. Center: in the X–H_2 complex the bond between the two hydrogen atoms is weakened and a binding to the X-nucleus is formed. The spin system is characterized by the mutual dipolar and spin–spin interactions of the three nuclei. The density matrix is evolving with time and consequently the spin state is not defined in the complex. Bottom: after the decay of the complex the spins are either in the *para*- or the *ortho*-state.

If one of these *para*-H_2 molecules reacts with the catalysts, a molecular complex of the type X–H_2 is formed, either by covalent binding or by the formation of hydrogen bonds or by unconventional bonds of the η^2-type. The three spins form a triangle, which is characterized by the two distance vectors r_{I1S} and r_{I2S} and the angle β between these distance vectors. In this complex an evolution of the initial density matrix occurs. In the course of this evolution a partial conversion of the *para*-state to the *ortho*-state occurs. When the bound state decays, this density matrix is transferred to the free dihydrogen state. Here fast phase relaxation destroys all coherences between the *para*- and the *ortho*-state and only the projections of the density matrix on the *para*- and *ortho*-subspaces survive. In other words, a part of the *para*-hydrogen is converted to *ortho*-hydrogen. In principle, one could also envision the opposite situation, namely that all molecules are prepared initially in the *ortho*-state. In this case part of the *ortho*-hydrogen is converted to *para*-hydrogen by the same mechanism. Finally we wish to note that thermodynamic effects are not included in the model. In a thermodynamic treatment which is beyond the scope of this paper, the calculated conversion rates will finally lead to a thermodynamic equilibrium between the *para*- and *ortho*-hydrogen.

The rest of the paper is organized as follows: first, the theory of the nuclear spin assisted spin conversion is presented. Then, after a brief discussion of the numerical methods, the numerical results are presented and discussed.

Theory of nuclear spin assisted *ortho*/*para*-H_2 conversion

In the following the model of the *ortho*/*para*-H_2 conversion in a three spin model is described. A detailed discussion of the density matrix formalism employed here is given in the original paper[51] and the review article[55] and will not be repeated here.

The kinetic model for the description of the *ortho*/*para*-H_2 conversion is similar to the calculation of stimulated nuclear polarization (SNP) in zero field by Dvinskikh *et al.*[56] It is assumed that the hydrogen molecules greatly outnumber the possible binding sites on the surface. In this situation, after a short initial period all binding sites on the surface will be occupied by hydrogen molecules. If τ_c is the average lifetime of a hydrogen molecule on a surface site, this lifetime is correlated with the decay rate k_{ab} of the bound state *via*:

$$k_{ab} = \frac{1}{\tau_c} \tag{1}$$

Moreover, due to the size of the exchange interaction J_{HH} in the gas state and the large excess of gaseous H_2, we can neglect off-diagonal elements of the density matrix of the gas state. In other words there are no coherent superpositions of the *ortho*- and *para*-states,

In the bound state, the dynamics of the spins of the hydrogen molecule are governed by the following zero field Hamiltonian (I_1, I_2: spin operators describing the H_2; S: operators describing the third spin on the surface):

$$\hat{H}_a = \vec{I}_1 \tilde{\mathrm{D}}_{1\mathrm{S}}\, \vec{S} + J_{1\mathrm{S}}\, \vec{I}_1 \vec{S} + \vec{I}_2\, \tilde{D}_{2\mathrm{S}}\, \vec{S} + J_{2\mathrm{S}} \vec{I}_2 \vec{S} + \vec{I}_1 \tilde{D}_{2\mathrm{S}} \vec{I}_2 + J_{\mathrm{II}} \vec{I}_1 \vec{I}_2 \tag{2}$$

Note that this Hamiltonian is the same for the hetero ($S \neq I_k$) and homonuclear ($S = I_k$) case. For the H_2 gase state, the spin Hamiltonian is given as:

$$\hat{H}_{HH} = J_{HH}\, \vec{I}_1 \vec{I}_2 \tag{3}$$

The description of the dynamics of the system is most easily done employing a Liouville space formalism. Here the state of the system is described with a system density matrix ρ, which is a vector in the Liouville space. The coherent evolution is controlled by the Liouville super operators L_a and L_{HH}, which are related to the Hamiltonians by the well known relation ($\hat{E}_k$: unity operators of Hilbert space k, the tilde denotes a complex conjugate operator):

$$\hat{\hat{L}}_a = \hat{H}_a \otimes \hat{\tilde{\hat{E}}}_a - \hat{E}_a \otimes \hat{\tilde{\hat{H}}}_a \tag{4}$$

and

$$\hat{\hat{L}}_{HH} = \hat{H}_{HH} \otimes \hat{\tilde{\hat{E}}}_{HH} - \hat{E}_{HH} \otimes \hat{\tilde{\hat{H}}}_{HH} \tag{5}$$

In the free gas phase the *para*-H_2 or in the *ortho*-H_2 state are the eigenstates of the spin Hamiltonian. The corresponding density matrices are:

$$\rho_{\mathrm{para}}(0) = \frac{1}{4}|E\rangle - \frac{1}{2}\left(|2I_{1x}I_{2x}\rangle + |2I_{1y}I_{2y}\rangle + |2I_{1z}I_{2z}\rangle\right). \tag{6}$$

$$\rho_{\mathrm{ortho}}(0) = \frac{3}{4}|E\rangle + \frac{1}{2}\left(|2I_{1x}I_{2x}\rangle + |2I_{1y}I_{2y}\rangle + |2I_{1z}I_{2z}\rangle\right). \tag{7}$$

As a starting point we assume for simplicity that all hydrogen molecules are prepared in the *para*-state, for example by suitable cooling of the system, and that the S spin is unpolarized. After binding to the surface this initial density matrix evolves under the influence of the Liouville super operators and decays with the rate k_{ab} back into the gas phase, resulting in the following differential equation (for simplicity, phase relaxation in the bound state is neglected):

$$\frac{\mathrm{d}}{\mathrm{d}t}|\rho_a) = -2\pi i \hat{\hat{L}}_a |\rho_a\rangle - k_{ab}|\rho_a\rangle = -\hat{\hat{M}}_a |\rho_a\rangle \tag{8}$$

The solution of this equation is:

$$|\rho_a(t)\rangle = \exp(-\hat{\hat{M}}t)\left|\rho_{\mathrm{para}}(0)\right\rangle \tag{9}$$

Due to the size of the exchange interaction J_{HH} in the gas state, we don't need to take the coherences between *para* and *ortho* functions, created in the bound state, into account and only the projections on the *para* and *ortho* subspaces need to be calculated. Employing the projection operators on the *para*-state $(\Gamma_{\mathrm{p}}|$ and on the *ortho*-state $(\Gamma_{\mathrm{o}}|$, the changes of the population of the *para* and *ortho* subspaces are given by the following expressions ($(\Gamma_\xi| = (\Gamma_{\mathrm{o}}|$ or $(\Gamma_{\mathrm{p}}|$, respectively):

$$\frac{\mathrm{d}}{\mathrm{d}t} n_\xi = k_{ab}(\Gamma_\xi|\rho_a(t)). \tag{10}$$

To calculate the overall change we have to integrate these expressions over the time:

$$\Delta n_\xi = k_{ab} \int_0^\infty (\Gamma_\xi|\rho_a(t))\mathrm{d}t. \tag{11}$$

Inserting the expression for the density matrix (eqn (9)) gives:

$$\Delta n_\xi = k_{ab} \int_0^\infty \left(\Gamma_\xi\right| \exp\left(-\hat{\hat{M}}t\right)|\rho_{\mathrm{para}}(0))\mathrm{d}t. \tag{12}$$

Since $\hat{\hat{M}}$ does not depend on time we can evaluate the integral

$$\begin{aligned} \Delta n_\xi &= k_{ab}\left(-\left(\Gamma_\xi|\hat{\hat{M}}^{-1} \exp\left(-\hat{\hat{M}}t\right)|\rho_{para}(0)\right)\right)\Big|_0^\infty \\ &= k_{ab}\left(\Gamma_\xi|\hat{\hat{M}}^{-1}|\rho_{para}(0)\right) \\ &= k_{ab}\left(\Gamma_\xi|\left(k_{ab} + 2\pi i\hat{\hat{L}}\right)^{-1}|\rho_{para}(0)\right) \\ &= \left(\Gamma_\xi|\left(1 + 2\pi i\hat{\hat{L}}/k_{ab}\right)^{-1}|\rho_{para}(0)\right). \end{aligned} \tag{13}$$

Replacing the decay rate of the bound state k_{ab} by its lifetime τ_c, the final result for the number of created *ortho*-H_2 molecules per one *para*-H_2 molecule is:

$$\Delta n_{\mathrm{o}} = \left(\Gamma_{\mathrm{o}}|\left(1 + 2\pi i\hat{\hat{L}}\tau_c\right)^{-1}|\rho_{para}(0)\right) \tag{14}$$

Numerical methods

All calculations were performed in the Matlab 6.0 environment using a laboratory written program. The Zeeman product functions of a three-spin system were chosen as base functions for the matrix representation of the Hamiltonians. In all calculations a three spin 1/2 system was employed, however the program allows for an arbitrary S-spin.

The Liouville space base functions of the Liouville space were constructed from the Hilbert space base functions and the Liouville super operator was expressed in these base functions and combined with the decay rate to the free state to the dynamic super operator $\hat{\hat{M}}$. This super operator is inverted and eqn (13) is calculated for the *para*- and the *ortho*-state.

Results and discussions

Numerical results

Before going into detail, first some general features of the calculations will be discussed. From eqn (14) it is evident that the rate of conversion depends on the product of the Liouville super operator and the lifetime of the bound state. The size of the elements of the Liouville super operator depends on the energy differences in the Hamiltonian, *i.e.* on the transition frequencies. Thus, eqn (14) states the expected result that the lifetime of the system must be long enough to allow for a change of the eigenstates of the Hamiltonian of the free H_2. Typical dipolar interactions of protons are on the order of a few kHz (for example the heteronuclear coupling between a proton and a ^{15}N nucleus with 2 Å distance in a hydrogen bond) and *ca.* 200 kHz (homonuclear dipolar interaction between two protons in a η-bonded transition metal complex with 0.84 Å distance, like the recently studied Kubas complex.[54,57,58] Thus the lifetimes of the bound state should be on the order of 1 ms, to allow for an efficient conversion. Accordingly, all calculations were performed with 1 ms as the lifetime of the bound state.

When the H_2 molecule binds to the substrate, either covalently or *via* hydrogen bonding, several different scenarios can render the two hydrogen atoms inequivalent, namely (i) the distances between the S-spin and the two hydrogens differ strongly; (ii) the distances are equal, but the angle between the dipolar vectors SI_1 and SI_2 is different from zero; (iii) the S-spin is also a hydrogen atom, which is in an η-bond to one of the I spins and the J_{SI}-coupling is the main source of the inequivalence of the two hydrogens. Such a situation could also be possible in a liquid.

In the following the numerical results for these different scenarios are presented: in all calculations initially only a population of the *para*-state is assumed. The figures show the relative amount of *ortho*-H_2 as a function of the various input parameters, which is a measure for the efficiency of the spin conversion. First the case of negligible spin–spin couplings J_{ii} between the two I spins is analyzed. This is the most often encountered situation, for example in most hydrogen bonded or covalently bound systems, where the quantum exchange coupling is strongly quenched and only weak magnetic J-couplings survive.[52]

Calculation of the *ortho*/*para*-H_2 conversion in situations where the two hydrogens are in different binding situations. The most basic situation is that both hydrogens are in different bonds, for example by addition to a $^{13}C{=}^{12}C$ double bond. In this situation the distances between the S spin and the two hydrogen atoms (I spins) are in general different and as a result the strength of the dipolar coupling between the S and the I spins are different. The angle between the two dipolar vectors is the angle between the two bond directions. In these situations the distance between the two hydrogens will be long and thus their dipolar coupling d_{ii} will, in general, be weak. Fig. 2 shows surface plots of the calculation of the *ortho*/*para*-H_2 conversion as a function of the strength of the dipolar couplings between the S spin and the I_1 spin D_{1S} and the dipolar coupling between the S spin and the I_2 spin D_{2S} for different angles β between the SI_1 and the SI_2 dipolar vector. For the interaction between the two I spins a small coupling of $d_{ii} = 1$ kHz was arbitrarily chosen. Along the main diagonal ($D_{1S} = D_{2S}$) the spins I_1 and I_2 are equivalent and the plane spanned by the main diagonal and the vertical axis is a symmetry plane of all figures. The case of collinear vectors, *i.e.* $\beta = 180°$, is the only one where no spin conversion is obtained along the main diagonal for non-zero couplings. In all other cases for $\beta > 0$ spin conversion is obtained for non-zero dipolar couplings along the main diagonal. Moreover, in all these cases after an initial growth of the spin conversion a plateau value is obtained for couplings which are larger than the decay rate of the bound state. The height of this plateau depends on the angle between the two dipolar vectors.

Calculation of the *ortho*/*para*-H_2 conversion for symmetric binding situations. The second important situation is that both protons are symmetrically bound to the same S spin. Examples of such a situation are metal dihydride complexes which are important intermediates in catalytic reactions. In these systems the homonuclear coupling d_{ii} between in the two hydrogen atoms can become very large (10^5 Hz). The dipolar coupling constants to the S spin are equal and only the angle between the two dipolar vectors and the strength of the coupling determine the efficiency of the spin conversion. Fig. 3 was

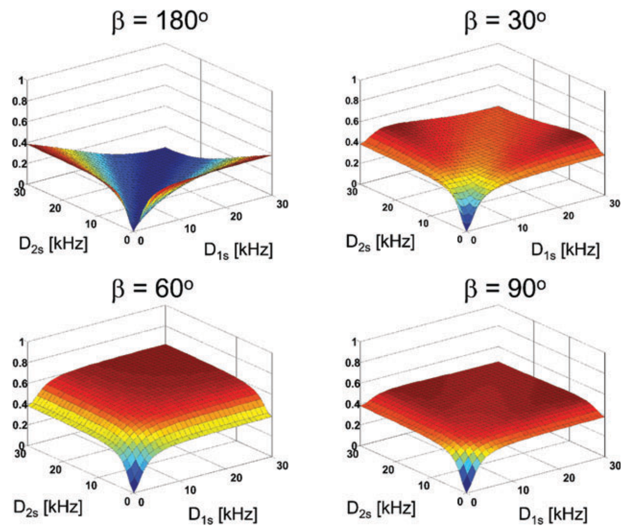
$\beta = 180°$ $\beta = 30°$ $\beta = 60°$ $\beta = 90°$

Fig. 2 Calculation of the *ortho*/*para*-H_2 conversion as a function of the strength of the dipolar couplings D_{1S} and D_{2S} for different angles β between the two dipolar vectors.

calculated for four different dipolar couplings between the two protons, namely $d_{ii} = 1$ kHz, $d_{ii} = 10$ kHz, $d_{ii} = 50$ kHz and $d_{ii} = 200$ kHz. Shown is the efficiency of the conversion as a function of the strength of the dipolar interaction d_{IS} and the angle β between the bond directions. The calculations reveal that the conversion efficiency depends only weakly on the strength of the homonuclear dipolar coupling. For all non-zero coupling strengths and non-collinear bond directions an efficient spin conversion is found. The efficiency of the spin conversion exhibits two maxima. The positions of these maxima vary between 54° and 63°, respectively 126° and 117°, depending on the strength of the homonuclear dipolar interactions. Between these maxima there is a shallow minimum at non-collinear bond direction = 90°.

Calculation of the *ortho*/*para*-H_2 conversion in the presence of strong exchange couplings J_{II}. In this section the case of strong exchange couplings is analyzed. Examples for this situation are several non-conventional transition metal dihydride complexes where quantum mechanical exchange interactions result in large values of J_{II}. In these complexes both protons have the same distance to the transition metal ion and thus the same coupling d_{IS}. The basic situation is equivalent to the previous case, which corresponds to the case $J_{II} = 0$. Fig. 4 displays, similar to Fig. 3, the spin conversion as a function of dipolar coupling and the angle between the two bond directions for several values of J_{II}. It is evident that even the moderate value of $J_{II} = 10$ kHz, which is less than the dipolar interaction and can be easily reached in a transition metal dihydride complex; has a strong impact on the efficiency of the spin conversion and reduces the rate of the spin conversion to *ca.* 50%. Stronger exchange interactions nearly completely quench the spin conversion, as shown in the second example with $J_{II} = 50$ kHz.

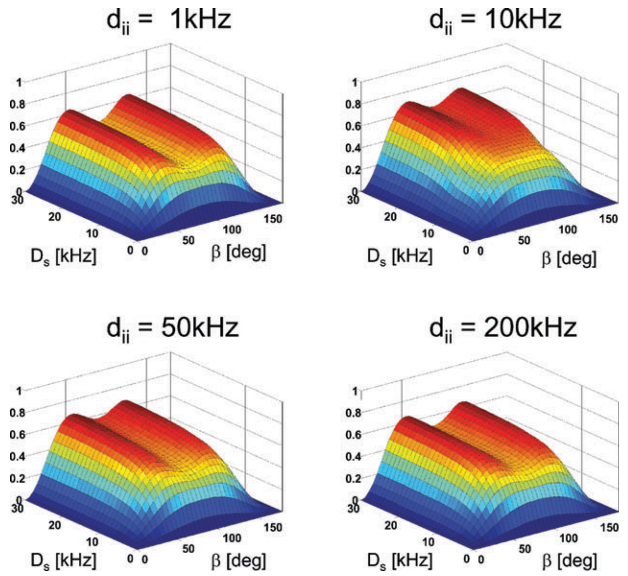

Fig. 3 Calculation of the *ortho*/*para*-H_2 conversion as a function of the strength of the dipolar coupling D_S and the angle β in symmetrically bound systems.

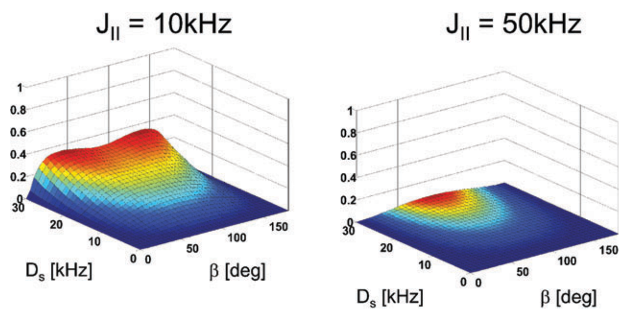

Fig. 4 Calculation of the *ortho*/*para*-H_2 conversion as a function of the strength of the dipolar coupling D_S and the angle β in symmetrically bound systems under the additional influence of an exchange interaction J_{II}. Note that even moderate exchange interactions cause a quench of the spin conversion.

Calculation of the *ortho*/*para*-H_2 conversion in the presence of strong exchange couplings J_{1S}. In this section the case of strong exchange coupling between the *S* spin and one of the *I* spins is analyzed. This situation is different to the previous ones because, setting all dipolar interactions to zero, the Hamiltonian of eqn (2) becomes isotropic, *i.e.* a pure liquid state NMR Hamiltonian.

Examples for this situation are in particular transition metal complexes where one of the two dihydrogen protons forms a η^2 bond with a third hydrogen (*i.e.* the *S* spin), already bound to the metal.

Fig. 5 shows surface plots of the calculation of the *ortho*/*para*-H_2 conversion as a function of the strength of the exchange interactions between the *S* spin and the I_1 spin J_{1S} and the exchange interaction between the *S* spin and the I_2 spin J_{2S}. All other interactions were set to zero in this calculation. Along the main diagonal ($J_{1S} = J_{2S}$) the spins I_1 and I_2 are equivalent and the plane spanned by the main diagonal and the vertical axis is a symmetry plane of the figure. Here no conversion is found. For all other pairs of values J_{1S}, J_{2S} an efficient spin conversion is found.

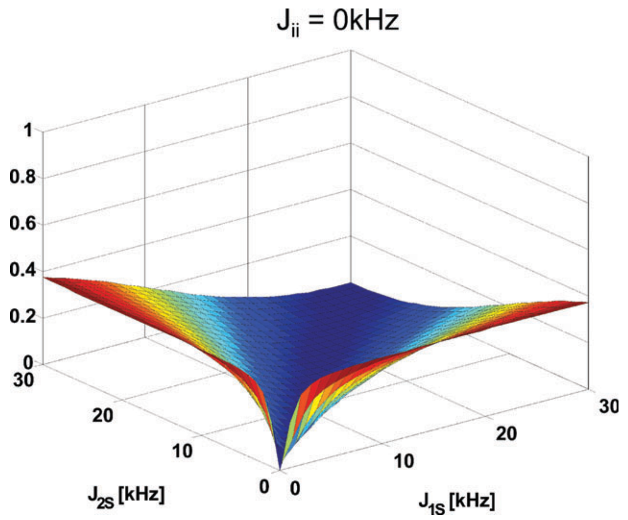

Fig. 5 Calculation of the *ortho*/*para*-H_2 conversion as a function of the strength of the spin exchange interactions J_{1S} and J_{2S} in a liquid like situation where all dipolar interactions are zero.

Discussion

The numerical calculations show that the quantum mechanical density matrix formalism allows the quantitative calculation of the *ortho*/*para*-hydrogen conversion in solid systems. Employing this formalism it is shown that dipolar spin–spin interactions cause an efficient conversion of *para*-hydrogen into *ortho*-hydrogen in the absence of a magnetic field. A necessary condition for the conversion is the breaking of the symmetry between the two hydrogen atoms. In the absence of a magnetic field this symmetry breaking is achieved by the dipolar interaction to a third spin *S*. This dipolar interaction must be present for a time which is on the order of the inverse of the strength of the dipolar interaction, *i.e.* typically for 10^{-5}–10^{-2} s or longer. Such a long lifetime necessarily implies the formation of a bound state between the dihydrogen and the *S* spin. This bound state can be formed either by covalent binding to the *S* spin or *via* hydrogen binding to the *S* spin or by η^2-binding to the *S* spin. Since the efficiency of the spin conversion depends on the bond angle, the observation of the conversion allows to draw conclusions about the structure of the complex formed during the conversion process.

It is worthwhile to note that the spin conversion depends only weakly on the strength of the dipolar interaction between the two hydrogen atoms. This result shows that for the conversion it is of no importance whether the two hydrogen atoms are bound to the same *S* spin or whether one is bound to the *S* spin and the second to a fourth atom, which can be spinless.

If only small or no exchange interactions between the two hydrogen spins are present efficient conversion is obtained for nearly all possible geometrical conformations of the three spin system. Only in the chemically very improbable case that all three spins are aligned along a line ($\beta = 180°$) and that both dipolar interactions are equal, which corresponds to a linear group of the type H–X–H, no spin conversion is obtained. In all other cases efficient spin conversion is observed. The situation is different in the third case. Here strong exchange interactions can be present. Even moderate exchange interactions strongly reduce the spin conversion rates and strong exchange interactions cause a complete quench of the spin conversion.

The quenching of the spin conversion by exchange interactions has important implications for the paramagnetic mechanisms of the spin conversion. In this mechanism an electron spin is coupled *via* hyperfine interaction to one of the two hydrogen atoms. From a mathematical point of view the hyperfine interaction is equivalent to the combination of a J_{1S} and D_{1S} interaction. Taking into account that typical hyperfine couplings are on the order of 1 to 1000 MHz, it follows that the exchange interaction between the two hydrogen atoms must be reduced to a value well below these hyperfine interactions to allow for an efficient conversion from *para*-hydrogen to *ortho*-hydrogen.

Finally it has also been shown that the nuclear spin exchange interactions can form an efficient conversion channel, permitting a spin conversion in liquids, where the dipolar interactions are removed by the fast reorientations of the molecules. Thus it should be feasible to achieve an *ortho*/*para*-conversion, for example, in liquid solutions of transition metal dihydrides.

Comparing the possible conversion efficiency of the paramagnetic conversion to the nuclear spin conversion it is evident that the paramagnetic mechanism is about three orders of magnitude faster than the nuclear spin mechanism, due to the larger couplings by the higher gyromagnetic ratio of the electron. On the other hand, however, the concentration of nuclear spins in general is several orders of magnitude higher than the concentration of paramagnetic impurities. Since the absolute conversion rate is proportional to the number of conversion sites n_X times the relative conversion rate, it follows that the faster conversion due to paramagnetic impurities is at least partially compensated by the higher density of nuclear spins. Thus even in systems with paramagnetic impurities the nuclear spin mechanism can be an efficient conversion channel. It would be interesting to try a quantitative comparison of these conversion channels for char-coal, the most often used conversion agents. Here it is generally assumed that paramagnetic impurities inside the char-coal are responsible for a magnetic spin conversion.[1] The question now is, how efficient this channel is compared to nuclear spin interactions to ^{13}C-nuclei, which have approximately 1% natural abundance.

We wish to note that this *ortho*/*para*-H_2 conversion could have interesting applications for the use of *para*-H_2 as an NMR polarization agents. In solids the normal PHIP effect at high magnetic field depends strongly on the relative orientation of the dipolar vectors to the magnetic field. Since PHIP is a differential effect, in non-oriented powder samples practically no net-polarization is created. In the absence of a magnetic field only the relative alignment of the three spins is important, as discussed in this paper. As a consequence of this fact in a non-oriented powder sample all *S* spins are influenced in the same way. If some local spin order of the *S* spin is created in the course of the *ortho*/*para*-H_2 spin conversion, it could in principle be possible to convert this spin order into a spin polarization by an ALTADENA like experiment. There are two ways how this spin order can be created, namely, either directly *via* the dipolar spin–spin interactions or indirectly *via* a chemical exchange of the three spins, as discussed in the previous paragraph. A detailed analysis of these applications is beyond the scope of this work.

The remaining question is: what happens if chemical exchange processes between the three spins occur. The zero field Hamiltonian of eqn (2) is symmetric with respect to heteronuclear and homonuclear interactions between the *S* spin and the two *I* spins. Thus the results calculated in this work are independent of the nature of the *S* spin. However, in real systems the possibility of chemical exchange processes between the three spins clearly exists. Here three different scenarios must be distinguished: (i) the pure heteronuclear case where the *S* spin is no hydrogen isotope and only the two *I*-spins of the initial *para*-hydrogen state can chemically exchange; (ii) the pure homonuclear case where all three spins are ^{1}H isotopes, which can mutually exchange; (iii) the homoisotopic case where the *S* spin is another hydrogen isotope, *i.e.* a ^{2}H or ^{3}H isotope, which can chemically exchange with the *I* spins, however causes a scrambling of the *ortho*- and *para*-states. For the calculation of these scenarios a more elaborate theory, which incorporates these different exchange processes, is necessary.

Summary and conclusion

In summary, it has been shown that the experimentally found *ortho*/*para*-hydrogen conversion in diamagnetic solids can be quantitatively explained as the result of dipolar interactions to nuclear spins, employing a quantum mechanical density matrix formalism of a three spin system. Numerical calculations show that for nearly all possible geometrical arrangements of the three spin system an efficient spin conversion is obtained. Only in the chemically improbable case of a linear group H–X–H no spin conversion is obtained. The efficiency of the spin conversion depends strongly on the presence of exchange interactions between the two hydrogens. Even moderate exchange couplings cause a quench of the spin conversion. Thus a sufficiently strong binding of the dihydrogen to the *S* spin is necessary to render the quenching by the exchange interaction ineffective.

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