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Novel Insights into the Mechanism of the *Ortho*/*Para* Spin Conversion of Hydrogen Pairs: Implications for Catalysis and Interstellar Water

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The phenomenon of exchange coupling is taken into account in the description of the magnetic nuclear spin conversion between bound ortho- *and* para-*dihydrogen. This conversion occurs without bond breaking, in contrast to the chemical spin conversion. It is shown that the exchange coupling needs to be reduced so that the corresponding exchange barrier can increase and the given magnetic interaction can effectively induce a spin conversion. The implications for related molecules such as water are discussed. For ice, a dipolar magnetic conversion and for liquid water a chemical conversion are predicted to occur within the millisecond timescale. It follows that a separation of water into its spin isomers, as proposed by Tikhonov and Volkov (*Science ***2002***, 296, 2363), is not feasible. Nuclear spin temperatures of water vapor in comets, which are smaller than the gas-phase equilibrium temperatures, are proposed to be diagnostic for the temperature of the ice or the dust surface from which the water was released.*

1. Introduction

The nuclear spin conversion between the two spin isomers of dihydrogen [Eq. (1)]:

$$ortho\text{-}H^{\uparrow}{-}H^{\uparrow} \rightleftharpoons para\text{-}H^{\uparrow}{-}H^{\downarrow} \quad (1)$$

is of high diagnostic value in science.[1–3] This is because the reaction is quantum-mechanically forbidden for the isolated molecule, but occurs under special but often unknown conditions. One can define three situations. In the first, a magnetic conversion occurs without bond elongation or breaking. For example, in solid dihydrogen dipolar magnetic nuclear interactions are responsible for an extremely slow spin conversion.[4] In the presence of unpaired electrons the conversion is accelerated by the magnetic hyperfine interaction.[5] The second situation also involves a magnetic conversion mechanism, but is assisted by an intermediate H–H bond elongation, for example, by binding to a transition metal center. Finally, in the third situation, a H–H bond splitting and re-formation with other hydrogen atoms occurs, which corresponds to a chemical spin conversion.[6] This overall process can be formally written as Equation (2):

$$H^{\uparrow}{-}H^{\uparrow} + H^{\downarrow}{-}H^{\downarrow} \rightleftharpoons 2\,H^{\uparrow}{-}H^{\downarrow} \quad (2)$$

It represents the analogue of the corresponding isotopic scrambling reaction [Eq. (3)]:

$$H{-}H + D{-}D \rightleftharpoons 2\,H{-}D \quad (3)$$

Many other molecules also contain equivalent hydrogen atoms in pairs, that is, form nuclear spin isomers, the most important being the water molecule. As in dihydrogen, the spin conversion in isolated water is forbidden or very slow.[7] Therefore, for water vapor in comets nonequilibrium *ortho*/*para* ratios have been observed, the origin of which is still unexplained.[8,9] Recently, Tikhonov and Volkov[10] have proposed to separate the water spin isomers by gas chromatography, and postulated that the spin conversion in condensed water is quenched.

These intriguing reports showed us that the spin conversion of hydrogen pairs still represents a physicochemical puzzle with important missing pieces. Previous[11] and recent preliminary[12] calculations in our laboratory indicated that one of the lacking pieces is the phenomenon of exchange coupling of dihydrogen pairs.[13] The aim of this Minireview is to reconstitute the puzzle as much as possible, and, therefore, to reach interesting conclusions concerning the feasibility of the separation of water spin isomers and the origin of the nonequilibrium *ortho*/*para* ratios in comets.

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2. Improved Mechanism of the Magnetic Nuclear Spin Conversion of Dihydrogen

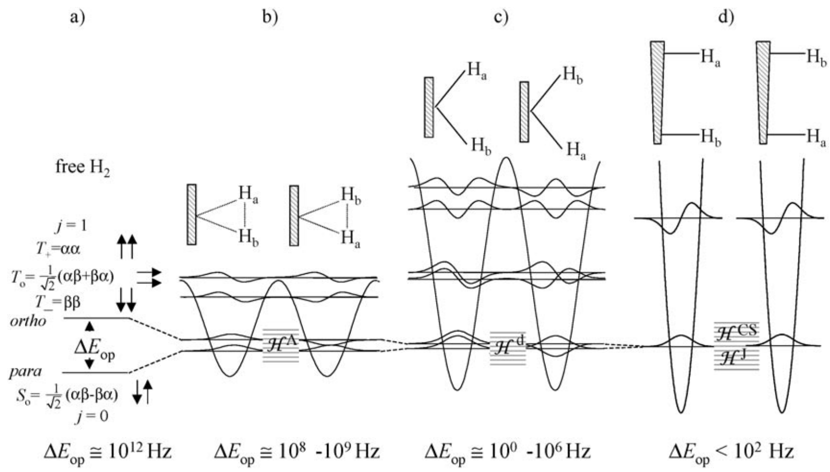

Figure 1. Improved mechanism of the magnetic *ortho/para* spin conversion of a bound dihydrogen pair. Binding involves an increase of the H–H distance and an increase of the barrier to rotation. The energy difference between the two lowest states ΔE_{op} decreases with the H–H distance. When ΔE_{op} is of the order of a given magnetic interaction, the corresponding Hamiltonian $\mathscr{H}$ mixes the singlet–triplet functions and induces spin conversion. $\mathscr{H}^A$: hyperfine interaction with a paramagnetic center; $\mathscr{H}^d$: dipole–dipole interaction; $\mathscr{H}^J$ scalar coupling interaction; $\mathscr{H}^{CS}$ chemical shielding interaction requiring an external magnetic field.

Figure 1 illustrates an improved mechanism of the magnetic spin conversion of a given dihydrogen pair in the absence of a chemical conversion. This mechanism is assembled from various experimental observations.[14,15] Free H_2 represents a three-dimensional quantum rotor, which has an equilibrium distance of 0.74 Å (Figure 1 a). *para*-H_2 corresponds to the manifold with even rotational quantum numbers *j*, characterized by combinations of symmetric rotational wave functions with the antisymmetric spin function. The odd values of *j* correspond to the *ortho*-H_2 states, and represent combinations of the antisymmetric rotational wave functions with the three symmetric nuclear spin functions. The energy difference between the two lowest rotational states of different symmetry is $\Delta E_{op} = 3.56 \times 10^{12}$ Hz for dihydrogen.[1] Under equilibrium conditions, the mole fraction of all *para* states is 0.25 at room temperature but about 0.5 at around 77 K. Note that the *ortho/para* ratio of the two lowest rotational states is 9:1 at room temperature because of the threefold rotational degeneracy of the lowest *ortho* state.

When dihydrogen is bound to a transition metal, it experiences a barrier to rotation which increases as the H–H bond length is increased (Figure 1 b–1 d). However, the quantum rotation is not immediately quenched but converted into a "rotational tunneling splitting". Thus, Kubas and co-workers[16] found dihydrogen configurations with distances of about 0.9 Å and values of ΔE_{op} of the order of 10^{11} Hz; the symmetries of the dihydrogen wave functions are preserved (Figure 1 b) and ΔE_{op} decreases as the H–H distance is increased. In the regime of the transition metal dihydrides exhibiting H–H distances around 1.7 Å,[13] ΔE_{op} is of the order of hertz to kilohertz. Here, its Boltzmann average has been called "exchange coupling J_{exch}", as it gives rise in the ^{1}H NMR spectra to similar splitting patterns as those of ordinary scalar magnetic couplings J_{magn}.[13] A temperature increase of J_{exch} arises from the formation of accessible dihydrogen states.

In ref. [11] the magnetic spin conversion of dihydrogen pairs induced via the chemical shift interaction $\mathscr{H}^{CS}$ in the presence of a magnetic field was described by some of us using the quantum-mechanical density matrix formalism. This conversion is associated with unusual enhanced absorption and emission lines labeled as *para*-hydrogen induced polarization (PHIP).[17–19] The calculated PHIP spectra were in good agreement with the observed ones, thus indicating the validity of the density matrix approach used. If exchange couplings are small, the established theory of longitudinal relaxation may also be used to describe the spin conversion.[20] We have extended our calculations to the case where an external magnetic field is absent, that is, where hyperfine, dipolar, or scalar magnetic interactions are operative.[12] These calculations show that each interaction can mix the nuclear singlet–triplet spin functions of dihydrogen pairs, and hence lead to a magnetic spin conversion efficiently, only if the expectation value of the corresponding Hamiltonian $\langle \mathscr{H} \rangle$ is larger or of the order of the energy difference between the *ortho* and *para* states, that is, if [Eq. (4)]

$$\langle \mathscr{H} \rangle \gtrsim \Delta E_{op} \tag{4}$$

This mixing of nuclear spin states is symbolized in Figure 1 by the hatched areas labeled with the various mixing spin Hamiltonians. Thus, an efficient catalyst of the magnetic spin conversion not only provides a suitable magnetic interaction, but also reduces the value of ΔEop of the dihydrogen pair by elongation of the H–H bond length. As the mismatch between the dipolar magnetic interaction $\langle \mathscr{H} d \rangle \cong 104$ Hz with ΔEop≅1012 Hz in solid dihydrogen is extremely large, the efficiency of the dipolar magnetic spin conversion is low, an insight which has not, to our knowledge, yet been recognized. By contrast, the mismatch is smaller for the hyperfine interaction $\langle \mathscr{H} A \rangle$ with unpaired electrons, which is of the order of 108–109 Hz. Nevertheless, the ortho/para conversion time of solid ortho-H2 near H atoms is still of the order of minutes.[5]

Our calculations predict a more efficient dipolar magnetic spin conversion in immobilized phases if ΔE_{op} is reduced to 10^3–10^4 Hz. In the liquid state, however, where $\langle \mathscr{H}^d \rangle$ is averaged to zero, the dipolar spin conversion mechanism may be less efficient. In this environment, scalar coupling $\mathcal{H}^J$ of hydrogen pairs in transition metal dihydrides to third spins is a source of magnetic spin conversion in the absence of an external magnetic field. Note that when the Larmor frequency of hydrogen is equal to ΔE_{op}, level crossing and hence spin conversion occurs.

3. Chemical Nuclear Spin Conversion of Dihydrogen

On the background of the improved spin conversion mechanism, we thought that it might be possible to incorporate and stabilize *para*-H_2 into transition metal dihydrogen complexes exhibiting large values of ΔE_{op} of the order of 10^{11} s^{-1}. However, careful studies showed that bond-breaking processes induced a chemical spin conversion and isotope scrambling. The latter had been observed by Kubas[21] for solid $W(CO)_3(P\mathit{i}Pr_3)_2(HD)$, which disproportionates at room temperature into a statistical mixture of the H_2, HD, and D_2 isotopologues. An example where both phenomena were observed together is polycrystalline Vaska's complex $Ir(CO)Cl(PPh_3)_2$ kept at 77 K under a 1:1 mixture of H_2 and D_2.[22] Under these conditions, gaseous *ortho*-H_2 was converted to *para*-H_2 and HD was also produced, which implies a bond-breaking process as illustrated schematically in Figure 2. Interestingly, the *ortho*/*para* ratios were determined by the temperature of the cold catalytic crystal surfaces and of the gas in close contact with these surfaces that led to the production of *para*-H_2; the latter then diffused into the upper warm parts of the NMR tube where the conversion was not operative. In other words, the nuclear spin temperature of the dihydrogen gas produced was around 77 K, whereas the equilibrium temperature was about 300 K.

4. Nuclear Spin Conversion of Water

In a qualitative way, the scheme of Figure 1 is valid for all molecules containing equivalent hydrogen atoms in pairs, such as water. Therefore, let us discuss the implications of the above findings for this molecule. Tikhonov and Volkov[10] observed a time-dependent enrichment of *ortho*-water vapor leaving a chromatographic column filled with porous materials. It was proposed that *para*-H_2O is preferentially adsorbed by the surfaces of the chromatography material without subsequent conversion into *ortho*-H_2O. This interpretation implies that the rotational states of *para*- and *ortho*-H_2O are preserved after adsorption, that is, that water does not experience on the surface a barrier to rotation which could prevent the conversion. This may be realized in the case of a weak physisorption, but not in the case of chemisorption via hydrogen bonding, which is the usual state of water on surfaces (Figure 3 a).[23] Hydrogen bonding introduces a substantial barrier to rotation and quenches the quantum rotation, which enables the dipolar magnetic spin conversion if the residence time on the surfaces is long enough and protons or other magnetically active nuclei are present in the surface. In water ice, a similar situation is realized. The protons of many immobilized water molecules form an infinitely large nuclear dipolar coupled spin system. As molecular rotations in ice are slow and incoherent,[24] ΔE_{op} is quenched and the dipolar conversion is operative.

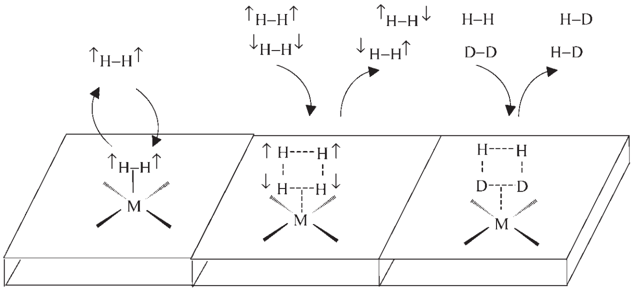

Figure 2. Mechanism of the chemical spin conversion of dihydrogen on surfaces containing a transition metal, according to ref. [22]. The magnetic spin conversion is suppressed (left) because of a large value of ΔE_{op} associated with short H···H distances in a dihydrogen complex. At least two dihydrogen molecules are necessary for the chemical spin conversion that is associated with the corresponding isotope scrambling reaction.

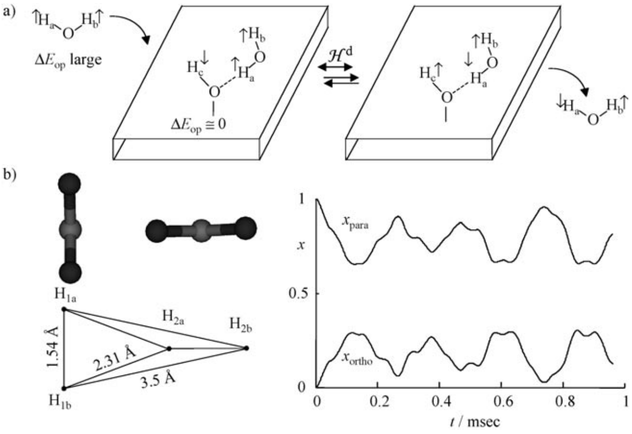

Figure 3. a) Magnetic spin conversion of water through dipolar interactions during immobilization via hydrogen bonding on a hydrophilic surface.
b) Model density matrix calculation of the dipolar magnetic spin conversion of a water dimer, which exhibits an arrangement typical for ice.[12] Starting from an initial pure *para* state, very fast creation of the *ortho* state within 100 μs and oscillation between the *para* and *ortho* states is observed. The *ortho*/*para* equilibrium is not reached, as relaxation was not included in the calculation.

To obtain an idea of the corresponding timescale for the latter, we performed a preliminary model density matrix calculation[12] of the dipolar magnetic spin conversion of an immobilized water dimer exhibiting a geometric arrangement typical for ice (Figure 3 b). At time $t = 0$ the two water molecules were arbitrarily prepared in the *para* state. We observe that the dipolar interaction leads to an oscillatory *para*/*ortho* conversion in the kilohertz range with conversion times of about 100 μs. To obtain a rate process and rate constants, larger spin systems have to be considered as well as the adsorption and desorption processes. Nevertheless, the calculations show that the conversion will be fast on a cold dust surface containing nuclear spins, in water ice at 77 K, where Tikhonov and Volkov[10] stored various water fractions, or in the cold water ice of comets.

Therefore, in analogy to the case of dihydrogen discussed above, we propose that the *ortho*/*para* ratio of water vapor released from a cold surface such as ice or any other material will reflect the temperature of the surface and of the gas phase close to the surface. After the release a higher vibrational, rotational, and translational temperature may be adopted by intermolecular collisions. This would explain the finding that the nuclear spin temperatures of water vapor in comets are around 30 K, whereas the equilibrium temperatures are above 50 K.[8,9] Thus, water vapor carries the information of the temperature of the surface from which it was released. These nuclear spin temperatures remain unaltered as in the gas phase, where both the magnetic and the chemical conversion are suppressed. This interpretation is corroborated by the recent finding that *para*-formaldehyde is converted to *ortho*-formaldehyde by surface adsorption.[25] We interpret this finding as being a result of dipolar spin conversion in the temporarily immobilized molecule, where ΔE_{op} is quenched and the dipolar interaction is operative.

Finally, in pure liquid water proton exchange proceeds via autoprotolysis into H_3O^+ and OH^- and by subsequent proton transfers.[26] From the rate constants of the individual proton-transfer steps measured by Meiboom by NMR spectroscopy of ^{17}O-enriched water[27] and the ionic product of water, one can calculate that the lifetime of a proton in pure liquid water is about one tenth of a millisecond at 298 K or shorter in the presence of acidic and basic impurities, whereas the deuteron lifetime in D_2O is about three times longer.[26] The question now arises of whether proton exchange can proceed without spin exchange, as has been proposed by Tikhonov and Volkov.[10] Firstly, this proposition ignores the fact that the original NMR measurement of Meiboom[27] is not a measurement of *proton* but of *spin* exchange. Secondly, for dihydrogen, no case of isotope scrambling has been observed to our knowledge which does not also involve a chemical spin conversion exhibiting similar or slightly larger rate constants, because of an additional magnetic spin conversion or a kinetic isotope effect. Therefore, liquid *para*- or *ortho*-water is unstable and will immediately equilibrate, thus preventing separation of the spin isomers.

5. Conclusions

In conclusion, the addition of quantum exchange and other missing pieces of the puzzle to the spin conversion of dihydrogen pairs provides novel insights, which will trigger a number of new calculations, experiments, and applications in the future.

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Keywords: exchange coupling · hydrogen · interstellar chemistry · spin conversion · water chemistry

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Supporting Information

Novel Insights into the Mechanism of the ortho/para Spin Conversion of Hydrogen Pairs: Implications for Catalysis and Interstellar Water

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Supporting Information

The conversion from the *para*- to the *ortho*- state necessitates either both a breaking and reformation of chemical bonds (chemical mechanism) or alternatively strong magnetic interactions, which are larger or at least of equal size as the exchange coupling J_{exch} as described in the text. They can break the exchange symmetry of the two protons and the symmetry adapted *para*- and *ortho*-states are no longer the eigenstates of the system.

Since such magnetic interactions are absent in the gas-phase and liquid phase, there exists no efficient magnetic conversion in these phases. In the case of ice however, the situation is different. Here the exchange coupling J_{exch} is strongly quenched by hydrogen bonding and the leading interactions are the intra- and intermolecular dipolar interactions. Since they couple the proton spins of the water molecules to a practically infinite spin-system, an exact calculation of the spin dynamics is not possible and one has to study simple model systems. The most model is a four spin system consisting of a set of two nearest neighbor water molecules taken out of the ice crystal.

In the absence of an external magnetic field the relevant spin Hamiltonian is the sum of the Hamilton operators of the individual water molecules plus the dipolar coupling Hamilton operator of the different water molecules:

$$\hat{H} = \hat{H}_a + \hat{H}_b + \hat{H}_{ab}$$

with

$$\hat{H}_a = \hat{I}_a \tilde{D}_a \hat{S}_a + J \hat{I}_a \hat{S}_a$$

$$\hat{H}_b = \hat{I}_b \tilde{D}_b \hat{S}_b + J \hat{I}_b \hat{S}_b$$

and

$$\hat{H}_{ab} = \hat{I}_a \tilde{D}_{II} \hat{I}_b + \hat{I}_a \tilde{D}_{IS} \hat{S}_b + \hat{S}_a \tilde{D}_{SI} \hat{I}_b + \hat{S}_a \tilde{D}_{SS} \hat{S}_b$$

Here the $\hat{I}_k$ and $\hat{S}_k$, $k=a,b$ denote the spin operators of the two protons in water molecule a and b. $\tilde{D}_a$ and $\tilde{D}_b$ are the intramolecular dipolar interaction tensors and the $\tilde{D}_{II}, \tilde{D}_{IS}, \tilde{D}_{SI}, \tilde{D}_{SS}$ are the intermolecular dipolar interactions tensors.

For the study of the conversion from the *para*- to the *ortho*- state a density matrix formalism is employed. As initial condition we assume that the system is in a pure *para*-state. For an individual water molecule the density matrix of the *para*-state is given by

$$\hat{\rho}_{k,para} = \frac{1}{4}\hat{E}_k - \frac{1}{2}(2\hat{I}_{\mathrm{kx}}\hat{S}_{\mathrm{kx}} + 2\hat{I}_{\mathrm{ky}}\hat{S}_{\mathrm{ky}} + 2\hat{I}_{\mathrm{ky}}\hat{S}_{\mathrm{ky}}).$$

The initial density matrix is a pure para state of both molecules:

$$\hat{\rho}(0) = \hat{\rho}_{para} = \hat{\rho}_{1,para} \otimes \hat{\rho}_{2,para}$$

This initial density matrix evolves under the influence of the dipolar Hamiltonian

$$\hat{\rho}(t) = \exp\left(-i\hat{H}t\right)\hat{\rho}(0)\exp\left(i\hat{H}t\right).$$

The fractions of *ortho*- and *para*-water are given by

$$x_{para} = \mathrm{Trace}\left[\hat{\rho}_{para}\hat{\rho}(t)\right] \text{ and } x_{ortho} = \mathrm{Trace}\left[\hat{\rho}_{ortho}\hat{\rho}(t)\right].$$

For the numerical calculations a laboratory written Matlab program is employed. The dipolar interaction tensors were determined from the geometry of an ice crystal. The calculation shown in Figure 3b was performed for $J_{exch} = 0$.