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Supporting Information

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

Hans-Heinrich Limbach,[1]* Gerd Buntkowsky,[2] Jochen Matthes,[1] Stefan Gründemann,[1] Tal Pery,[1] Bernadeta Walaszek,[1] and Bruno Chaudret[3]

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 $J_{exch} = 0$.