Mechanisms of Dipolar Ortho/Para-H$_2$O Conversion in Ice

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In this paper a possible explanation for an unexpected *ortho*/*para*-water ratio in the gas clouds
of comets is given. The description is based on the quantum-mechanical density matrix formal-
ism and the spin temperature concept. Only the nuclear spin system is treated quantum-mechani-
cally. Employing the model of a four spin system, created by two nearest neighbour water
molecules, spin eigenstates and their dynamics under the influence of their mutual dipolar
interactions are studied. It is shown that a fast conversion between *ortho*- and *para*-states occurs
on a msec time scale, caused by the intermolecular homonuclear magnetic dipolar interaction.
Moreover the spin eigenstates of water in an ice crystal are determined by magnetic dipolar
interactions and are not given by normal *ortho*- and *para*-H$_2$O states of gaseous water. As a
result of this the spin temperature of gaseous water evaporated from ice depends strongly on
its evaporation history and the *ortho*/*para*-ratio of water molecules are only an indirect measure
of the temperature of ice crystals from where they descend. This result could explain the
unexpected experimentally observed *ortho*/*para*-ratios in the clouds of comets.

1. Introduction

It is well known that the quantum mechanical exchange symmetry plays an
important role in the quantum mechanical structure of hydrogen molecules and
leads to the formation of two different spin isotopomers called *para*- and *ortho*-
hydrogen [1]. These two isotopomers are of high diagnostic value in chemistry

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[2,3] and biochemistry [4]. An important application of these quantum mechanical symmetry effects are the so-called "Para Hydrogen Induced Polarization" or short "PHIP" experiments [5,6]. If hydrogen gas (deuterium gas works similar) is kept at low temperatures (typically liquid nitrogen or below), it converts after some time into the energetically favorable *para*-hydrogen, for example by contact to paramagnetic species [1] or adsorption to nuclear spins [7]. These *para*-hydrogen molecules are in a pure nuclear singlet state, which is associated via the Pauli exclusion principle with the lowest rotational state. They are stable in liquid solutions [2,8]. Their high spin polarization can be utilized as an extremely sensitive monitor of the fate of hydrogen in catalytically induced hydrogenation reactions (see for example [3,9–29]).

These symmetry effects are not restricted to hydrogen and many other molecules as for example water, methane, formaldehyde or ammonia, which contain equivalent hydrogen atoms also form nuclear spin isotopomers. From the chemical and biological point of view the water molecule is the most important of these molecules. Recently, it was proposed that water spin isomers are separable by gas chromatography or producible by catalyzed reactions of *para*-hydrogen [30] and that the spin conversion in condensed water is quenched [31] and that adsorption properties of water depend on the spin state [32]. As in dihydrogen, the spin conversion between these spin isotopomers in isolated water is forbidden or very slow and the concentration ratio of the two isotopomers is observable [33]. This ratio is of high diagnostic value in astrophysics because it allows for remote measurements of the temperature in water clouds in interstellar space. For water vapor in comets non-equilibrium *ortho*/*para*-ratios have been observed the origin of which are still unexplained. [34–40] In these experiments the population ratio of the *para*- and *ortho*-states of water is employed as a measure for the spin temperature of the water vapor in the cloud of the comet. For example experiments showed for the comet C 2001 Q4 a typical gaseous water temperature of 30K [40]. This temperature is too low for an efficient sublimation of *para*-water from the ice of the comet. This rises the question to what extent the temperature of water vapors produced by comets does coincide with the temperature of ice in the comet and is it possible to simply take the *para*-/*ortho*-ratio as a measure of the surface temperature of the comet ice?

A first answer to this question was already given by Mumma et al. [35], which applies the concept of the nuclear spin temperature to this problem. The concept of a nuclear spin temperature is well known from magnetic resonance (see for example the monographs by Abragam and Goldman [41,42]). The main idea is to treat the nuclear spin energies, as for example the Zeeman energy or the magnetic dipolar energy, as independent thermodynamic reservoirs and associate individual temperatures to these reservoirs. Owing to the relatively weak magnetic couplings these reservoirs equilibrate in general only slowly among themselves or with the spatial degrees of freedom of the system (lattice temperature).

If the nuclear spin state and thus the population ratios do not change in the course of the sublimation it follows that the nuclear spin temperature of water

vapor is applicable as a measure of the temperature of ice inside of the comet [33]. In the course of the low density water vapor of comets these interconversion times are extremely long (see estimation by Mumma et al. [35]). However they already realized that no information of the effect of lattice bonding in the ice and the sublimation process on the *ortho/para*-ratio is available.

This leads directly to a second subtle problem related to this question, namely the identification of the relevant thermodynamic spin reservoir in the ice crystal. In gaseous water this question is readily answered, because the rotational degrees of freedom dominate the spin interactions and the energy associated with the *para/ortho*-splitting is by far the largest contribution to the spin Hamiltonian as discussed above. Early studies in the year 1932 of Giauque and Ashley [43] assumed that the same is true in ice, resulting in the existence of stable *para*-ice and *ortho*-ice molecules.

In the following we want to discuss the validity of this assumption and solve the question regarding the effect of lattice bonding and its impact on the *ortho/para*-ratio employing density matrix theory [44–46]. In a preceding paper some of us have reported already some preliminary results on this mechanisms of spin conversion in *para*-ice [47]. In the present work we now wish to show that the *para/ortho*-conversion is very fast inside the ice and only "frozen" outside the comet where water molecules exist as isolated vapor molecules. For this we give a detailed theoretical study of the conversion mechanism and the underlying quantum mechanical spin dynamics in an ice crystal, employing a simple model of two water molecules. As a result of these calculations we will find that the *para*- and *ortho*-states are no eigenstates of the water molecules in the ice crystal and only produced in the course respectively after the evaporation from the surface.

2. Theory

In the gas-phase no hindering potential acts on the rotational states of water molecules and they can be treated as quantum mechanical free rotors with the corresponding energy eigenstates, which split up in the *para*- and *ortho*-manifold. This is no longer the case when water molecules are in a bound state, for example by physi- or chemisorption to a surface, by hydrogen binding to another molecule or as part of an ice crystal. In this case a rotational hindering of the molecular reorientations is created. The most efficient reorientational motion in this potential is the rotation of the water molecule around its C_2-axis.

For a quantitative estimation of the changes of energy eigenfunctions and values caused by the hindering, we can write down a simple one dimensional Schrödinger equation for the rotation of a water molecule in a harmonic twofold potential:

$$-\frac{\hbar^2}{2\mu r^2}\frac{d^2}{d\varphi^2}\,|\,\Psi\rangle - V_0(1-\cos 2\varphi)\,|\,\Psi\rangle = E\,|\,\psi\rangle\,. \tag{1}$$

(a)   (b)

free H$_2$O   H$_2$O in Ice
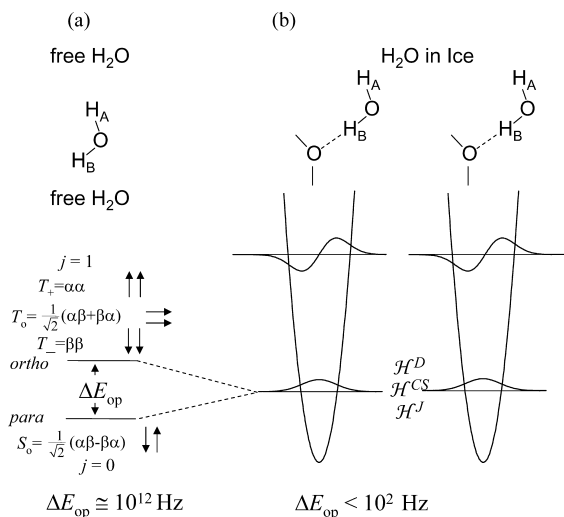
Fig. 1. Energy levels of *para*-H$_2$O and *ortho*-H$_2$O in the gas phase (a) and in the ice crystal (b). In the gas phase the water molecule is a free quantum rotor and the energy splitting between *para*- and *ortho*- states is $\Delta E_{op} \approx 4 \times 10^{11}$ Hz. In the ice crystal hydrogen bonding and other intermolecular interactions act as a hindering potential for the free rotation of the water molecule and quench the energy splitting between *para*- and *ortho*- states to values of the order $\Delta E_{op} \approx 10^{-2}$ Hz. As a result of this quenching spin interactions start to determine the fate of the states.

Here $2V_0$ describes the depth of the hindering potential, $r = 1.54$ Å is the distance of the two hydrogen atoms in the water molecule and μ is the reduced mass of the water molecule. This differential equation is of the Matthieu type.

The corresponding eigenfunctions split into two sets of eigenfunctions (see Fig. 1), namely cosine type functions $|C_n(\varphi)>$ and sine type functions $|S_n(\varphi)>$

$$\left| C_n(\varphi) \right\rangle = \sum_{k=0}^{\infty} a_{n,k} \left| c_k(\varphi) \right\rangle \text{ and } \left| S_n(\varphi) \right\rangle = \sum_{k=1}^{\infty} b_{n,k} \left| s_k(\varphi) \right\rangle , \tag{2}$$

which are linear combinations of the base functions

$$\left| c_0(\varphi) \right\rangle = \frac{1}{\sqrt{2\pi}}$$

$$\left| c_k(\varphi) \right\rangle = \frac{1}{\sqrt{2}} \left(\left| \Psi_k(\varphi) \right\rangle + \left| \Psi_{-k}(\varphi) \right\rangle \right) = \frac{1}{\sqrt{\pi}} \cos(k\varphi) \tag{3}$$

$$\left| s_k(\varphi) \right\rangle = \frac{1}{\sqrt{2}i} \left(\left| \Psi_k(\varphi) \right\rangle - \left| \Psi_{-k}(\varphi) \right\rangle \right) = \frac{1}{\sqrt{\pi}} \sin(k\varphi)$$

The ground state wave function is always a cosine type state with even symmetry and the first excited state is always a sine type function with odd symmetry.

The energy differences between different $C_n(\varphi)$ and $S_n(\varphi)$ depend strongly on the depth of the potential $2V_0$ and varies between zero and the order of typical rotational μ– wave or IR transitions.

The amount of rotational hindering of the water molecules in ice can be estimated, employing the data of Wittebort et al. [48], which have shown that the activation energy of a molecular orientation of a water molecule (H$_2$O or D$_2$O) in ice is 13.3±0.2 kcal/mol (55.7±0.9 kJ/mol). This activation energy corresponds to a frequency of 1.4×10^{14} Hz. Employing this activation energy as an estimation of the depth of the rotational barrier of the water rotation, the difference between the lowest pair of eigenstates is estimated as 10^{-2} Hz by numerical solution of Eq. 1 and the energy difference between the lowest pair of eigenfunctions and the next pair is estimated as 1.5×10^{13} Hz.

It follows that at temperatures in the range of 100 K and below only the lowest pair of eigenstates is thermally populated. In this case, as was already realized by Dirac, for a system of two coupled spin-½ particles, the spin alone is able to characterize the four lowest eigenstates of the system [49]. For an individual gaseous water molecule the eigenstates are

$$
\begin{aligned}
|S_0\rangle &= \frac{1}{\sqrt{2}}\left(|\alpha\beta\rangle - |\beta\alpha\rangle\right) \\
|T_{+1}\rangle &= |\alpha\alpha\rangle \\
|T_0\rangle &= \frac{1}{\sqrt{2}}\left(|\alpha\beta\rangle + |\beta\alpha\rangle\right) \\
|T_{-1}\rangle &= |\beta\beta\rangle .
\end{aligned}
\tag{4}
$$

The $|S_0\rangle$ state couples to the symmetric ground *para*-state to form a singlet manifold and the $|T_k\rangle$ states couple to the odd *ortho*-state and form the triplet manifold. The corresponding density matrices of individual molecules are:

$$
\hat{\rho}_{para}(0) = \frac{1}{4}\left(\hat{E}\right) - \left(\hat{I}_{1x}\hat{I}_{2x} + \hat{I}_{1y}\hat{I}_{2y} + \hat{I}_{1z}\hat{I}_{2z}\right)
\tag{5}
$$

$$
\hat{\rho}_{ortho}(0) = \frac{3}{4}\left(\hat{E}\right) + \left(\hat{I}_{1x}\hat{I}_{2x} + \hat{I}_{1y}\hat{I}_{2y} + \hat{I}_{1z}\hat{I}_{2z}\right).
\tag{6}
$$

For the H$_2$O gas state, the individual water molecules can be treated as free quantum mechanical rotors. If J_g is the exchange coupling between the lowest *para*- and *ortho*-states of the free water rotor, these states can be completely described via a pure spin Hamiltonian, which is given as

$$
\hat{H}_g = J_g \vec{I}_1 \vec{I}_2 .
\tag{7}
$$

This spin-Hamiltonian commutes with the *para*- and *ortho*- density matrices.

The situation changes when the water is no longer gaseous but frozen. In this case on the one hand the molecules are no longer free rotors and their exchange coupling is extremely reduced to the magnetic coupling J_{HH}. On the other hand there are now additional magnetic dipolar interactions between the different protons which can alter the eigenfunctions of the system. The full spin-Hamiltonian for the description of the system is

$$
\hat{H} = \sum_k \vec{I}_k \tilde{D}_k \vec{S}_k + J_{H_2O}\sum_k \vec{I}_k \vec{S}_k + \sum_{k<l} \vec{I}_k \tilde{D}_{k_a l_a} \vec{I}_l + \sum_{k<l} \vec{I}_k \tilde{D}_{k_a l_b} \vec{S}_l + \sum_{k<l} \vec{S}_k \tilde{D}_{k_b l_a} \vec{I}_l +
$$
$$
\sum_{k<l} \vec{S}_k \tilde{D}_{k_b l_b} \vec{S}_l ,
\tag{8}
$$
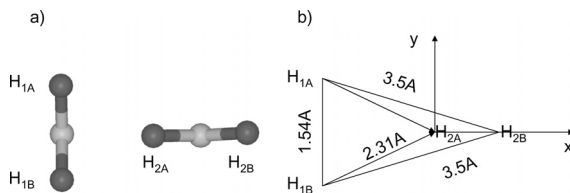
Fig. 2. Structure of two nearest neighbor water molecules in the ice crystal and the geometrical parameters employed in the calculations, taken from x-ray structure of ice.

where the sum runs over all water molecules in the crystal. In thermal equilibrium the density matrix of the system is given as

$$\hat{\rho}_{eq} = \frac{1}{Z} \exp\left(-\frac{\hat{H}}{k_B T}\right) \approx \frac{1}{\text{Trace}\left(\hat{1}\right)}\left(\hat{1} - \frac{\hat{H}}{k_B T}\right), \tag{9}$$

where Z is the partition function of the system.

Owing to the large density of protons in ice, in principle one would have to treat a nearly infinite spin system to study the stability of *para*-ice, which is not feasible. To reach a treatable level of complexity it is necessary to employ simple models of the ice structure. In the present calculations we employ a system of two nearest neighbor water molecules taken out of the ice structure, i.e. a four spin system (Fig. 2).

In the following the model of the conversion of *para*-H_2O to *ortho*-H_2O in this four spin system under the influence of homonuclear magnetic dipolar interactions and spin-spin couplings is developed. In our model of ice, the dynamics of spins of water molecules is governed by the following zero field Hamiltonian (I_1, S_1: spin operators describing the first water molecule; I_2, S_2: spin operators describing the second water molecule, D_1, D_2: dipolar interaction tensors of water molecule 1 and 2, D_{1n2m}: dipolar interaction tensors between the hydrogen atoms of two water molecules; J_{ice}: exchange coupling in a single water molecule):

$$\begin{aligned}
\hat{H} &= \vec{I}_1 \tilde{D}_1 \vec{S}_1 + \vec{I}_2 \tilde{D}_2 \vec{S}_2 \\
&\quad + \vec{I}_1 \tilde{D}_{1a2a} \vec{I}_2 + \vec{I}_1 \tilde{D}_{1a2b} \vec{S}_2 + \vec{S}_1 \tilde{D}_{1b2a} \vec{I}_2 + \vec{S}_1 \tilde{D}_{1b2b} \vec{S}_2 \ . \\
&\quad + J_{H_2O} \vec{I}_1 \vec{S}_1 + J_{H_2O} \vec{I}_2 \vec{S}_2
\end{aligned} \tag{10}$$

We assume that both molecules are initially in the *para*-H_2O state.

$$\hat{\rho}\left(0\right) = \hat{\rho}_{1,para} \otimes \hat{\rho}_{2,para} \ . \tag{11}$$

The coherent evolution of the density operator under the influence of the Hamiltonian is governed by the following equation of motion

$$\frac{d}{dt}\hat{\rho} = -i\left[\hat{H},\hat{\rho}\right]. \tag{12}$$

In this equation we have followed the NMR convention and set the constant $\hbar = 1$, which is equivalent to measuring energies in angular frequency units. Since the

Hamilton operator does not explicitly depend on time, the equation of motion of the density matrix can be solved with the help of the following unitary propagator

$$\hat{U}(t) = \exp(-i\hat{H}t) \, . \tag{13}$$

The time dependent density matrix is

$$\hat{\rho}(t) = \hat{U}(t) \cdot \hat{\rho}(0) \cdot \hat{U}^{-1}(t) \, . \tag{14}$$

Using $\hat{\rho}(t)$ the expectation value of any physical observable $\langle\hat{A}\rangle$ is given as:

$$\langle\hat{A}\rangle = Tr[\hat{A} \cdot \hat{\rho}(t)] \tag{15}$$

In the case of conversion of *para*-ice to *ortho*-ice we are interested in the relative amount of molecule pairs which are still both in the *para*-state or which both are in the *ortho*-state after time t. These numbers are proportional to the expectation values of the matrices

$$n_{para} = \left\langle \hat{\rho}_{1,para} \otimes \hat{\rho}_{2,para} \right\rangle \tag{16}$$

and

$$n_{ortho} = \left\langle \hat{\rho}_{1,ortho} \otimes \hat{\rho}_{2,ortho} \right\rangle . \tag{17}$$

Inserting the time dependent density matrix [14] gives

$$n_{para} = Tr\left[\left(\hat{\rho}_{1,para} \otimes \hat{\rho}_{2,para} \right) \cdot \hat{U}(t) \cdot \hat{\rho}(0) \cdot \hat{U}^{-1}(t) \right] \tag{18}$$

and

$$n_{ortho} = Tr\left[\left(\hat{\rho}_{1,ortho} \otimes \hat{\rho}_{2,ortho} \right) \cdot \hat{U}(t) \cdot \hat{\rho}(0) \cdot \hat{U}^{-1}(t) \right] . \tag{19}$$

For the further discussion it is very useful to employ a base set where the Hamiltonian Eq. 10 is diagonal. In this base the diagonal elements of the density matrix correspond to the populations of the energy eigenstates and the off-diagonal elements correspond to coherent superpositions of different eigenstates [50]. In this eigenbase the diagonal elements of the density matrix are constant

$$\rho_{mm}(t) = \rho_{mm}(0) \tag{20}$$

and the off-diagonal elements $m \neq n$ oscillate with the frequency $\omega_{mn} = E_m - E_n$

$$\rho_{mn}(t) = \rho_{mn}(0)\exp\left(-i\omega_{mn}t\right) \tag{21}$$

In this base, as a result of the time dependence of the density matrix, for short times t in general an oscillating behavior of the off-diagonal density matrix elements and thus the numbers of *ortho*- and *para*-molecules will be found. For larger waiting times, phase relaxation will cause the disappearance of the off-diagonal elements and only the diagonal elements survive. Thus the long time behavior of the numbers of *ortho*- and *para*-molecules is solely determined by the diagonal elements of the density matrix.

3. Numerical procedures

All calculations were performed in the MATLAB 7.1 environment employing laboratory written code. All simulations are done in a four spin system, consist-

ing of the four hydrogen atoms of the two nearest neighbor water molecules. In a
first step the magnetic dipolar interaction tensors are calculated from the distance
vectors between the four hydrogen atoms of the two water molecules. Next the
twelve cartesian single spin operators of the four hydrogen atoms are constructed
from the single spin ½ operators $\hat{\sigma}_\mu : \mu = x, y, z$ and the two-dimensional identity
operator $\hat{E}$

$$
\begin{aligned}
\hat{I}_{1,\mu} &= \hat{\sigma}_\mu \otimes \hat{E} \otimes \hat{E} \otimes \hat{E} \\
\hat{I}_{2,\mu} &= \hat{E} \otimes \hat{\sigma}_\mu \otimes \hat{E} \otimes \hat{E} \\
\hat{S}_{1,\mu} &= \hat{E} \otimes \hat{E} \otimes \hat{\sigma}_\mu \otimes \hat{E} \\
\hat{S}_{2,\mu} &= \hat{E} \otimes \hat{E} \otimes \hat{E} \otimes \hat{\sigma}_\mu
\end{aligned}
\tag{22}
$$

Employing these spin operators the matrix representation of the spin Hamiltonian
(Eq. 10), the initial density matrix (Eq. 11) and the detection operators for *para*-
and *ortho*-states are constructed. In the next step the Hamiltonian is diagonalized
and the eigenvector matrix of the Hamiltonian is employed to transform the
initial density matrix and the detection operators into the eigenbase of the Hamil-
tonian.

For long times the coherent oscillation of these off-diagonal elements disap-
pears by phase relaxation. To account for such a phase relaxation an empirical
phase relaxation time T_2 is employed. The J-coupling constant between the two
protons inside a water molecule is taken as free parameter, which is varied in
the calculations. The geometrical arrangement of the water molecules is shown
in Fig. 2.

4. Results and discussions

Before going into details some general features of the calculations will be dis-
cussed. From Eq. 14 it is evident that the speed of conversion depends on the
product of the transition frequencies and the waiting time. The frequencies are
given by the energy differences in the Hamiltonian, which depend on the inter-
and intramolecular dipolar interactions. Thus an efficient conversion will appear
after times determined by the inverse of the dipolar interactions. Moreover while
the amount of created *ortho*-H_2 will initially oscillate, these oscillations will die
out after a phase relaxation time T_2 and a stable finite value will be found, which
is determined solely by the diagonal elements of the density matrix.

4.1 Numerical results

In the following numerical results are presented: In all calculations initially only
a population of the *para*-state of both molecules is assumed. The figures show
the relative amount of *para*-H_2O and *ortho*-H_2O as a function of various input
parameters. They are measures for the efficiency of the spin conversion. They
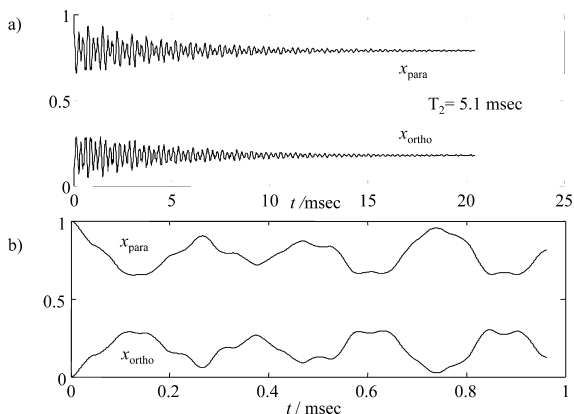
Fig. 3. Time dependence of the relative *para-* and *ortho*-H$_2$O concentrations for completely quenched tunnel splitting (J$_{H_2O}$=0 Hz). (a) Long time behavior. Oscillations are initially damped with a time constant T$_2$. (b) Initial part of the oscillations. Note that already after ca 100 µsec an efficient conversion has occurred.

are analyzed as a function of intramolecular spin-spin coupling J$_{H_2O}$ between two spins in a water molecule, which is taken as a free parameter to account for different tunnel splittings.

4.2 Para- ortho-H$_2$O conversion in the absence of a tunnel splitting

Figure 3a shows the dependence of the relative *para-* and *ortho*-H$_2$O concentrations on the time in the absence of any tunnel splitting or spin-spin coupling between the two hydrogen atoms on a single water molecule. Initially only *para-*H$_2$O is present. An oscillating behavior of the amount of created *ortho*-H$_2$O is observed. It is evident that after a very short time below one millisecond a substantial amount of *ortho*-H$_2$O is created. To emphasize this effect, Fig. 3b shows the short time behavior. The first maximum, where roughly 30% of *para-*H$_2$O is converted to *ortho*-H$_2$O, occurs already after ca. 100 µsec. Thus it is evident that the intermolecular homonuclear dipolar interaction indeed is capable to efficiently convert *para-*H$_2$O to *ortho*-H$_2$O.

4.3 Para- ortho-H$_2$O conversion as a function of the tunnel splitting

Since the tunnel splitting is formally equivalent to a magnetic J-coupling in the next step we study the dependence of the relative *para-* and *ortho*-H$_2$O concentrations on the time as a function of different sizes of the combined magnetic J-coupling and tunnel splitting or spin-spin coupling between the two hydrogen atoms on a single water molecule (Fig. 4). It is evident that for most J-couplings below 30 kHz an oscillating behavior of the amount of created *ortho*-H$_2$O is found. Fourier transformation of the signals reveals that in general several differ-
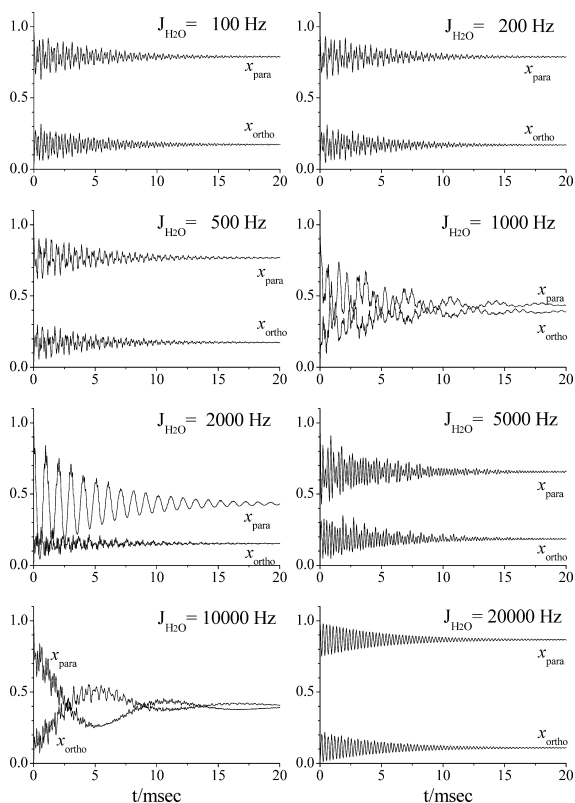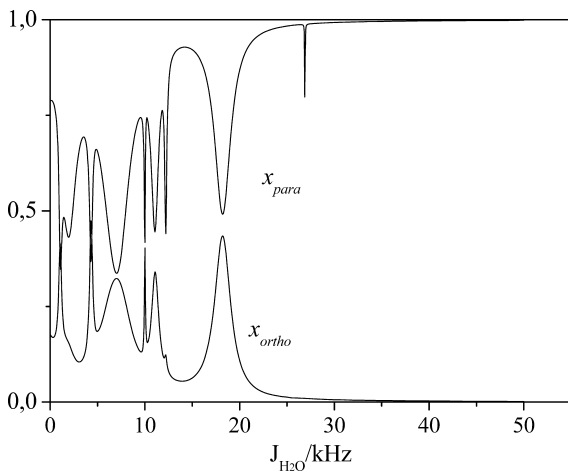
Fig. 4. Time dependence of the relative *para-* and *ortho-*H_2O concentrations for different sizes of the tunnel splitting $J_{H_2O}=0$. Note that different frequencies are inside the time signal and the different finite values.

ent frequencies are present in the time signals. The dominant oscillation frequency is not simply given by the tunnel splitting. Moreover also the end levels of the created *ortho-*H_2O have a complicated dependence on the size of the tunnel splitting (see Fig. 5). It is evident that the conversion curves consist of several broad and narrow maxima. Moreover above $J_{H_2O}=30$ kHz practically no conversion from *para-*H_2O to *ortho-*H_2O occurs anymore.

5. Discussion

The numerical calculations show that the quantum mechanical density matrix formalism allows the quantitative calculation of the *ortho/para*-water conversion in solid systems like ice. Employing this formalism it is shown that dipolar spin-spin interactions cause an efficient conversion of *para*-water into *ortho*-water in

Fig. 5. Dependence of the final relative *para-* and *ortho*-H$_2$O concentrations on the magnitude of the J$_{H_2O}$ coupling.
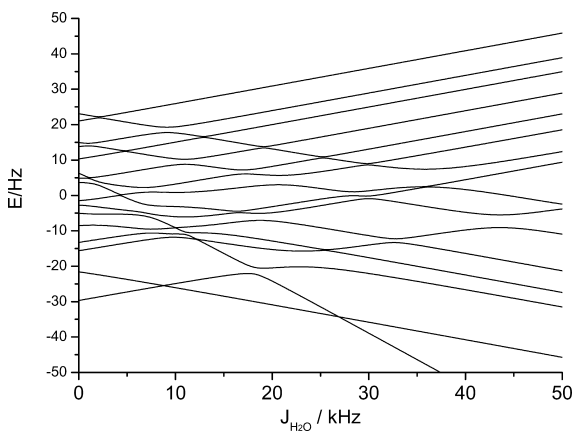
Fig. 6. Dependence of the spin energy eigenvalues on the magnitude of the J$_{H_2O}$ coupling.

the absence of a magnetic field. A necessary condition for the conversion is the breaking of the symmetry between the two hydrogen atoms in a water molecule by intermolecular dipolar interactions to neighboring water molecules. After a time which is on the order of the inverse of the strength of the dipolar interaction, i.e. 10^{-5}sec to 10^{-4}sec, an efficient spin conversion occurs by the dipolar interaction. The efficiency of the spin conversion depends strongly on the size of the tunnel splitting J$_{H_2O}$.

Figure 6 displays the dependence of the energy eigenvalues of the two water molecules on the size of the tunnel splitting, which is an measure. It is evident

that several level crossings (LC) and level anti crossings (LAC) are passed in the course of the variation of J_{H_2O}. Comparing the positions of these LC and LACs with the maxima in the conversion curve (Fig. 5) it is evident that efficient conversions mainly take place in the vicinity of crossings. Thus the maxima in the curve can be identified as a typical level crossing effect. Similar level crossing effects are also known from other types of spectroscopy, as for example optical nuclear polarization [51,52].

This result is not only important on its own, but it also helps us to draw conclusions on the fate of a *para*-water molecule which is sublimating on or evaporating from an ice crystal. In the case of sublimation as soon as the molecule is close to the surface it will feel both the electric (electric dipole moment and hydrogen bonds) and the magnetic (spin dipolar) interactions with the water molecules on the surface of the ice crystal. The electric interactions cause the presence of a rotational barrier for the molecule which strongly reduces the size of the tunnel frequency. As soon as the tunnel frequency is reduced below 30 kHz, a spin conversion from the *para*-state to the new eigenstates occurs. As a result of this spin conversion part of the *para*-molecules are converted into *ortho*-molecules and vice versa. In the case of evaporation on the other hand the fate of the initial spin state depends strongly on the speed with which this region of reduced rotational hindering is passed. While the general case is extremely difficult to analyze there are two limiting cases which can be analyzed.

In the case of a slow passage through this region the spin-states will *adiabatically* follow the curves of the energy eigenfunctions in Fig. 6 and conserve their populations. In the case of a fast passage a so-called *sudden change* will occur which mainly keeps the spin state intact during the evaporation. As a result of this fast transition the *ortho/para*-ratio and thus the spin temperature measured after the evaporation will be given by the relative projections of the full nuclear spin Hamiltonian on these states.

In both limiting cases the *ortho/para*-ratio in the gas phase is determined by two factors, namely the quantum mechanical state of the ice-molecules which is determined by the magnetic dipolar interactions in the ice and the evaporation history of the ice molecule and is thus only an indirect measure for the temperature inside of the ice.

A quantitative estimation of the dependence of ice-temperature and *ortho/para*-ratio would necessitate a more sophisticated thermodynamic model of the ice which is beyond the scope of the current paper.

6. Summary and conclusion

In summary it has been shown that the spin eigenstates of water in an ice crystal are determined by the magnetic dipolar interactions and are not given by the normal *ortho*- and *para*-H_2O states of gaseous water. Moreover the homonuclear magnetic dipolar interactions in ice crystals provide also an efficient conversion

mechanism between *ortho-* and *para-*H$_2$O inside the ice. This shows that no stable *para-*ice can exist and there will always be a fast interconversion from *para-* to *ortho-*molecules and back.

Thus the magnetic dipolar energy between the hydrogen atoms in the ice crystal is the relevant thermodynamic reservoir for the nuclear spin temperature and will determine the spin temperature of the evaporated water molecules. However, the actual spin temperature will depend not only on the spin temperature of the ice, but also on the evaporation history of the water molecules, owing to the changes of the quantum mechanical eigenstates in the process of evaporation. Thus the *ortho/para-*ratios of water molecules in the gas phase are only an indirect measure of the temperature of the surface temperature of the ice crystals from where they descend and the fate of the molecule in the course of the evaporation has to be taken into account. This result could be the explanation for the unexpected experimentally observed *ortho/para-*ratios in the clouds of comets [34–40].

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