

A FIRST STEP FOR THE UNDERSTANDING OF DISEQUILIBRATED ORTHO TO PARA RATIOS FOUND IN SPACE : STUDIES OF NUCLEAR SPIN CONVERSION OF H₂O IN RARE GAS MATRICES

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Abstract.

As a first step before studying ices of astrophysical interest, we have investigated the parameters involved in the nuclear spin conversion of water isolated in rare gas matrices at low temperatures (4.2 K). In these environments, the water molecule rotates almost freely and is able to perform translational oscillations within the cage made of rare gas atoms. We present here a study, in the mid-infrared, of H₂O in neon, argon, krypton and xenon matrices. In all the matrices, we observed an acceleration of the nuclear spin conversion as the concentration of water in the sample increased. Calculations performed by our group show clearly that intermolecular magnetic interactions are responsible for this concentration dependence. The intermolecular process is found to slow down from neon to xenon because the lattice parameter continuously increases from neon to xenon. For diluted samples we measured times between 100 and 700 minutes depending upon the rare gas atom. It is then surprising that these times observed in cryogenic matrices are much shorter than months estimated in ice by Tikhonov & Volkov (2002) at 77 K.

1 Introduction

Water molecules represent the major species liberated as the comets approach close to the Sun. Recent observations using infrared or sub-millimetric sensitive telescopes (Crovisier 2006) allow to access to the quantum states of the molecules and specially to their nuclear spin states. In case of water, molecules are named *ortho* or *para* according as the spins of the protons are parallel (total nuclear spin $I=1$) or anti-parallel (total nuclear spin $I=0$). In gaseous phase, each rotational state is associated with only one of the nuclear magnetic species and in the high temperature limit (≥ 50 K), due to spin degeneracy 1/4 of the molecules are *para*, while 3/4 are *ortho*. Below 50 K, the OPR (*ortho* – *to* – *para*) ratio at the Boltzmann equilibrium becomes strongly temperature dependent. From the OPR measured in different comets, so-called spin temperatures have been extracted and compared to the temperatures associated with other degrees of freedom of the molecules (kinetic, rotational, vibrational). The results (Crovisier 1998, 2006; Kawakita et al. 2006; Bonev et al. 2007) showed that for most of the molecules observed in different comets (C/1995 O1-Hale Bopp, C/2001 A2-LINEAR, C/2001 Q4-NEAT,...), the measured spin temperatures are spread around a mean value of 30 K while rotational temperatures are between 25 and 100 K (Bonev et al. 2007). The origin of these non equilibrated nuclear spin states is not understood yet but, if this disequilibrium have been kept constant for billions of years, the OPR would be a clue of the temperature formation of the protosolar nebulous. In this context, it is important to know the possibility for different cold media like gas (Tudorie et al. 2006), solid (Tikhonov & Volkov 2002), or surface (Tudorie et al. 2007) to conserve or not nuclear spin states disequilibria at low temperatures. We studied first nuclear spin conversion (NSC) in rare gas solids for which measurements were performed but not completely explained yet (Michaut et al. 2004 and references therein).

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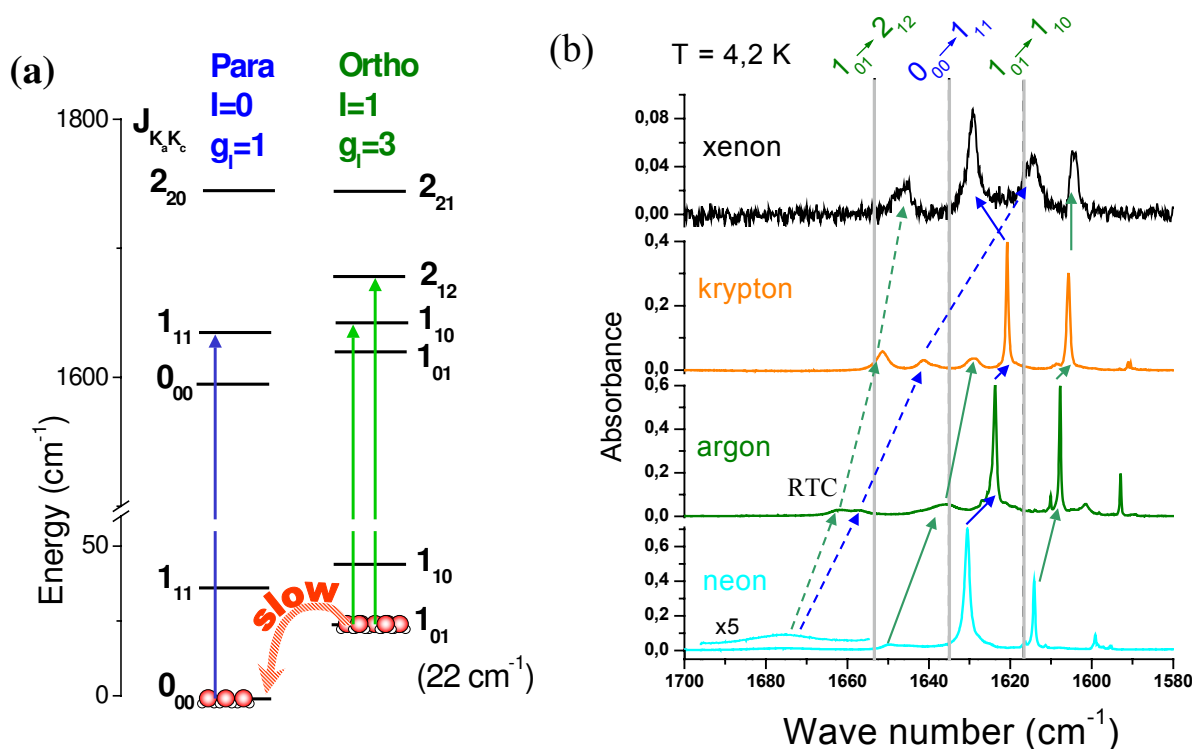


Fig. 1. Vibrational bending mode ν_2 of water. (a) Populated rotational energy levels of water molecules at low temperature and main infrared transitions observed in rare gas matrices at 4.2 K (b) Experimental spectra recorded at 4.2 K just after a fast cooling from 20 K in the different matrices. The vertical lines indicate the position of the rovibrational lines for the free molecule. RTC =Rotation-Translation-Coupling.

2 Experimental procedure

The experimental details have been described elsewhere (Pardanaud et al. 2007). The solid sample is prepared using the "spray on" technique. The gaseous mixture of H_2O (doubly distilled and outgassed), and RG=Rare Gas (Air Liquide Company, > 99.999% purity), is prepared by standard manometric procedures in a stainless steel and pyrex device. This gaseous sample is deposited onto a gold-coated copper plane mirror cooled to temperatures ranging from 4.2 K (for neon) to 35 K (for xenon) by a closed-cycle helium cryogenerator. After deposition (at 20 K for argon), the sample is first cooled down slowly to preserve optical quality of the polycrystalline layer. The light from a FTIR Bruker IFS 113v spectrometer is reflected on the mirror and thus goes twice through the solid sample before being analysed. The spectra are recorded with 0.15 cm^{-1} resolution. Due to the weakness of the electric interactions between the molecule and the atoms of the cage, it is known that the molecule can vibrate, and quasi-freely rotate (Michaut et al. 2004). The mid-infrared spectrum of the molecule is then similar to the one expected in gas at low temperature. The Figure 1.a shows the rovibrational energy diagram of water molecules in the bending region ν_2 . As H_2O is an asymmetric rotor, rotational energy levels are labeled using 3 quantum numbers : the total angular momentum J and its projections K_A and K_C on the principal inertial axis of the molecule. The figure 1.b shows typical spectra of H_2O isolated in the various rare gas matrices at 4.2 K, recorded just after a fast cooling from 20 K, for a concentration $H_2O/RG=1/2000$. As NSC is slow the OPR value is frozen from 20 K to 4.2 K : thus the water molecules are not in Boltzmann equilibrium at that time.

The time evolution (Michaut et al. 2004) shows that the *ortho* lines decrease to the benefit of the *para* lines. As the integrated intensity of a line is proportional to the fractional population of the molecules on the initial energy level of the transition, following the time evolution of the intensity allows to measure the needed time

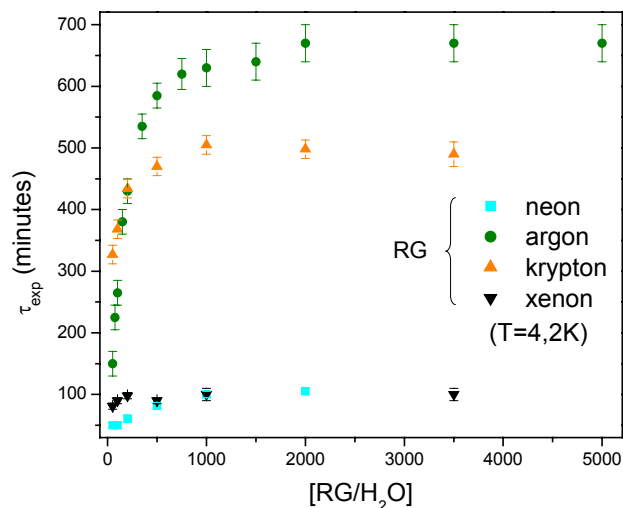


Fig. 2. Evolution of the experimental time of conversion with water dilution at 4.2 K for Ne, Ar, Kr and Xe.

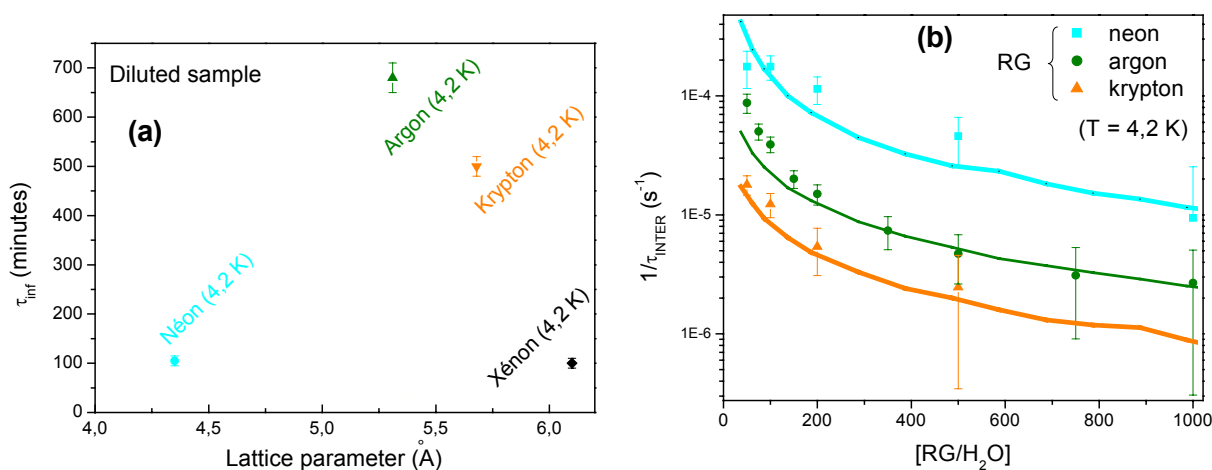


Fig. 3. Comparison of the NSC in the four matrices. (a) Diluted sample. (b) Concentrated samples. The intermolecular part of the experimental data (see text) are compared to the contributions of magnetic intermolecular interactions (lines) calculated using spin-spin interactions between water molecules randomly spread in the solid.

for the system to recover the Boltzmann equilibrium. The experimental data are fitted using single exponential decay and the characteristic conversion time τ_{exp} can be measured in various experimental conditions (Michaut et al. 2004; Pardanaud et al. 2007; Abouaf-Marguin et al. 2007).

3 Results and discussion

We have shown previously that nuclear spin conversion of water in argon is strongly dependent on the dilution from 2000 down to 50 at 4.2 K. We calculated the possible contribution of magnetic interactions between water molecules embedded in the sample. We used a numerical procedure to randomly distribute water molecules in a perfect argon lattice. The magnetic dipoles of the two protons of one molecule produce an inhomogeneous magnetic field between the two protons of a neighbouring interacting molecule. This magnetic gradient allows then the molecules to experience Rabi oscillations between the two nuclear spin states. Collisions with the rare gas atoms of the cage are then necessary to make the molecules to transfer their rotational energy to the matrix

through phonons emission. This last mechanism allows the molecules to be finally trapped in the lowest energy level and thus to be converted. Calculations show that the conversion through this process is concentration dependent at low dilution ($Ar/H_2O \leq 2000$), as this process is distance dependent. Calculations also shows that for high dilutions ($Ar/H_2O \geq 2000$), these interactions can not contribute efficiently to the NSC and can not explain the conversion time of $\tau_{inf} = 680 \pm 30$ minutes measured experimentally. It seems then that for each concentration, two mechanisms coexist. The second mechanism must be concentration independent and responsible for the nuclear spin conversion for molecules infinitely diluted in the sample. To eliminate *external* effects, we checked the influence of different parameters like IR radiation from the spectrometer, presence of a metallic sample holder, or atmospheric impurities. We showed (Abouaf-Marguin et al. 2007) that no one of these parameters can explain the observed behavior. Thus the nuclear spin conversion is due to an "intrinsic" interaction with the matrix. Solid argon does not have magnetic isotopes but it hinders the rotation of the H_2O molecule. Then the only explanation of this conversion is the enhancement of intramolecular spin rotation coupling by the matrix so that the lowest *ortho* and *para* energy levels are connected, which is strictly forbidden for the isolated molecule.

We have also checked, by changing the rare gas, the influence of a small change of the environment. Figure 2 shows the evolution of τ_{exp} in function of the dilution of water in the sample for the four rare gas matrices. For higher concentrations ($Ne/H_2O \leq 500$, $Ar/H_2O \leq 2000$, $Kr/H_2O \leq 1000$) the NSC constant vary strongly leading to the conclusion that the intermolecular process is also active in Ne and Kr. Figure 3.b shows the evolution with RG/H_2O of the conversion constant due to magnetic intermolecular interaction, denoted as $1/\tau_{inter}$ and obtained by assuming that intra and intermolecular mechanisms can be decoupled following the simple law : $1/\tau_{exp} = 1/\tau_{inf} + 1/\tau_{inter}$. For a given dilution, results from the model and experiments show a good agreement. NSC from intermolecular origin is more active in Ne, than in Ar, than in Kr, because the mean distance between water molecules increases from Ne to Kr, as does the lattice parameter. However, only a tendency has been pointed out in Xe where no clear variation has been found even when $Xe/H_2O=50$.

Figure 3.a shows the matrix effect on NSC in the diluted domain : a factor of ~ 7 on the conversion times is encountered without any kind of continuity. The difference of mass from Ne to Xe and the presence of magnetic isotopes in Kr and Xe may play an important role.

4 Conclusions

To conclude, we showed that nuclear spin conversion is very sensitive to magnetic interactions as well as to the environment of molecules. As the decrease of mean distances between molecules in the solid enhances the NSC, this process might be very fast in pure ice. However as rotation is blocked in ice, the mechanism to liberate the excess energy might be more complicated. So it is difficult to extrapolate to pure ice which is the suitable medium for direct applications to astrophysics. Efforts are made by our group to investigate NSC in ice and to understand why conversion times observed in cryogenic matrices are so short compared to the durations of months estimated in ice at 80 K (Tikhonov & Volkov 2002).

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