Equilibration des états de spins nucléaires dans l'espace : apports des études en laboratoire

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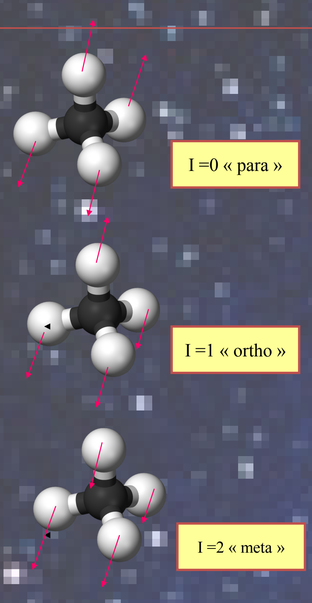
ANR-09-BLAN-0066-01

1. Spin Isomers

Due to the Pauli exclusion principle, hydrogenated molecules such as H_2O, having equivalent atoms exist in different nuclear spin configurations (also called "spin isomers") corresponding to different values of the total nuclear spin I.

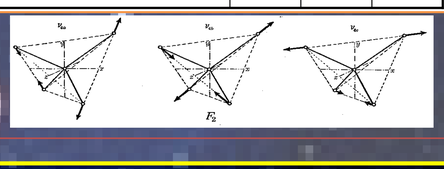


CH_4

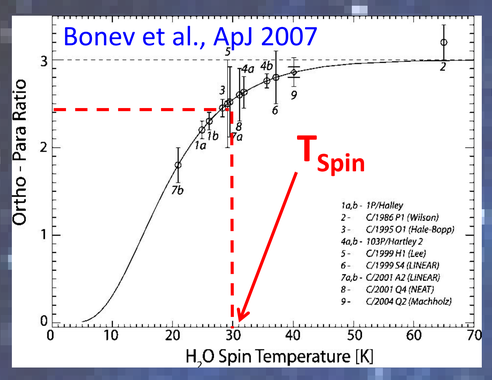
Due to the half-integer value of the spin of the proton, methane possesses 3 spin isomers with total spin I= 0, 1 ou 2. Each spin configuration has specific symmetry characters (E, F, or A) of the symmetry operations of the group T.

species	E	F	A
Total nuclear spin	0	1	2

species	A_1	F_1	$E+F_2$
Rotational Quantum Number J	0	1	2



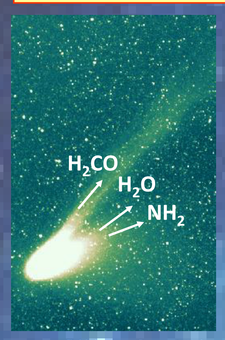
2. Astrophysical context



OBSERVATIONS
nuclear spin statistic out of equilibrium

Physical origin of the spin temperature ?

COMETARY ATMOSPHERES



Large field image of comet Hale-Bopp taken the 17th of february 1997
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H_2O	(C/1999 H1) :	$T_{spin} \approx 30$ K
	(C/2001 A2) :	$T_{spin} = 23 \pm 4$ K
	(Hale-Bopp) :	$T_{spin} = 28 \pm 2$ K
NH_3	(Hale-Bopp) :	$T_{spin} = 26$ K
CH_4	(C/2001 Q4) :	$T_{spin} = 33 \pm 3$ K

$100\ K > T_{rot} > 50\ K$

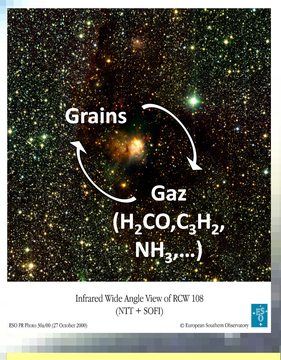
$T_{spin} \sim 30$ K

Solid-gas interface
Hydrogenated species
Hypothesis: NSC forbidden on the cometary core

Memory of the spin states equilibrium at the formation date of grains or molecules ?

« … The small diversity of the nuclear spin temperatures and lack of clear correlation between T_{spin} and chemical composition in several comets are consistent with the hypothesis that T_{spin} reflects the temperatures in the presolar nebula. » Kawakita et al, Astrophysical Journal 2006

INTERSTELLAR CLOUDS



NH_3	(L1157) : $T_{spin} \sim 18 - 25$ K	Umemoto et al, Astrophys. J. (1999)
H_2CO	(L723,...) : $T_K \sim 10$ K	Dickens et al, Astrophys. J. (1999)
C_3H_2	(TMC-1) : OPR < 2 (correlated to chemical evolution)	Morisawa et al, Astrophys. J. (2006)
H_2O	(young star TW Hydrae) : $T_{spin} \sim 14$ K	Hogerheijde et al Science (2011)

ADMITTED ASSUMPTION = NSC FORBIDDEN IN GAS PHASE BUT FAST ON GRAINS WHEN THE MOLECULE IS FORMED

Solid-gas interface
Hydrogenated species
Hypothesis: Fast NSC on the grain surfaces

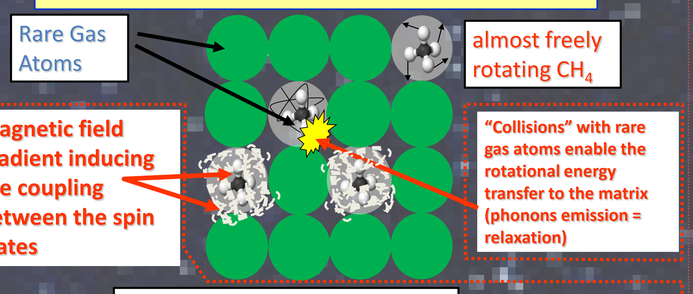
What kind of information about the « history » of the molecule could we deduce from measurements of ratios between spin isomers?
Shall we say that $T_{spin}=T_{formation}$?

« …,The O/P ratio after a reaction reflects neither the temperature of reaction fields nor the excess energy of the reaction, but simply reflects the conservation of angular momentum. » Morisawa et al, Astrophys. J. (2006)

« … Radiative conversion between spin isomers is not allowed in the gas phase, preserving the OPR for long time scales. Gas-phase formation of water occurs through exothermic reactions leading to an OPR of 3. On grains, water forms and survives at low temperatures, and it is tempting to equate T_{spin} with the grain temperature. However, the energetics of water formation and ortho-to-para exchange on grains are poorly understood, and the water OPR may be changed by photodesorption.[…] Provided that spin temperatures reflect formation histories, the different T_{spin} inferred for the water ice in TW Hya (<13 K) and solar system comets (>20 K) indicates a similar mixing of volatiles throughout the entire solar nebula, blending water formed at >50 K and an OPR of 3 with water formed at 10 to 20 K and an OPR < 1 probed by our observations. In this case, the range of Tspin values of the cometary inventory reflects the stochastic nature of transport and mixing. » Hogerheijde et al Science (2011)

3. Nuclear Spin Conversion of Rotating Molecules in Solid State

CONVERSION MECHANISM

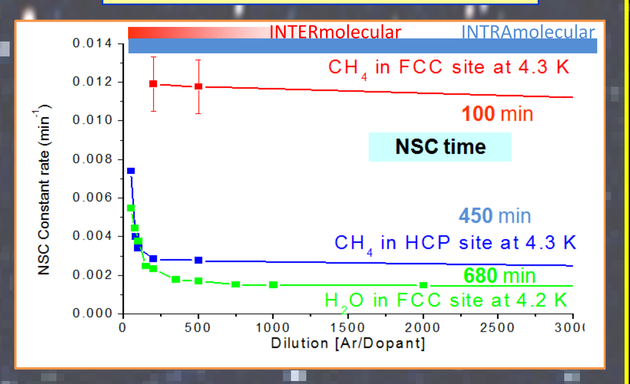


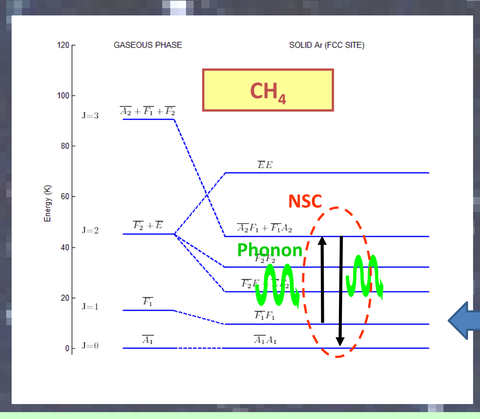
Source of MAGNETIC COUPLING

INTERmolecular
CH_4-CH_4 (spin-spin, spin-rotation)
CH_4- *magnetic impurities* (O_2)

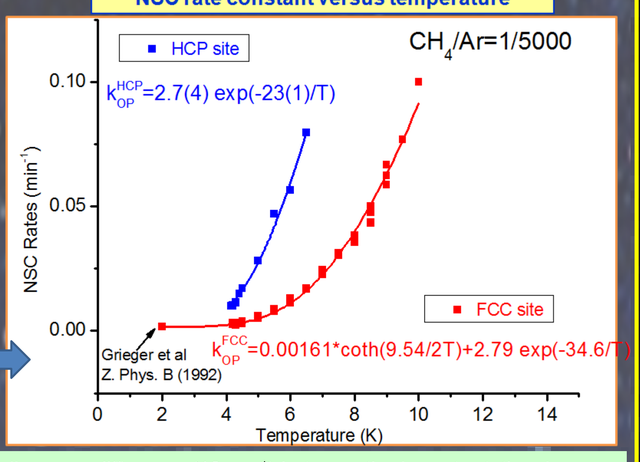
INTRAmolecular
Spin-Spin
Spin-Rotation

NSC rate constant versus dilutions





NSC rate constant versus temperature



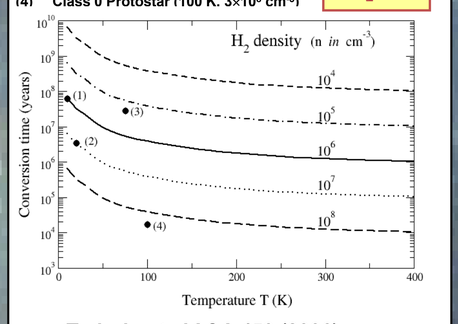
NSC conversion is faster for methane than for water presumably due to the small energy difference (10 cm^{-1}) between the lowest rotational energy levels of *ortho* (J=1) and *meta* (J=0) species (to be compared to the 22 cm^{-1} between *ortho* and *para* states of water).
Strong differences are observed for CH_4 trapped in Face Centered Cubic and Hexagonal Close-Packed sites. They are also presumably due to the energy spacing between rotational states in the different sites. In the Ar matrix (FCC site), the rotational states of the molecules are distorded by electric interactions. The J=2 level is splitted in 3 sublevels with F2 and E symmetry. Analysis of the temperature dependence using multiphonon Orbach model shows that in FCC site, NSC is enhanced by the degeneracy of the state J=3. In case of HCP site, the NSC is dominated by coupling of the J=1 state to a state lying 23/1.44=16 cm^{-1} above. Temperature dependence of NSC in Ar matrix seems to follow a two phonons Orbach mechanism (Scott and Jeffries, Phy. Rev. 127, 32 (1962)). Sequentially, one phonon is absorbed, the molecule makes a rotational transition to an intermediate state before going to the final state with the emission of one phonon.

Nuclear Spin Conversion is fast in solid state and depends of the energetic structure of the molecule and the intreractions with the environment. (Pardanaud *et al* J. Mol. Spec 2009, Abouaf-Marguin *et al* CPL 2009, Pardanaud PhD 2007, Lekic PhD 2011)

4. Nuclear Spin Conversion of Molecules in the Gas Phase

4 typical environments
(1) Prestellar Core (T = 5-10 K, $n(H_2) = 10^6$ cm^{-3})
(2) Protoplanetary disk(20 K, 10^7 cm^{-3})
(3) PDR (75 K, 2×10^5 cm^{-3})
(4) Class 0 Protostar (100 K. 3×10^8 cm^{-3})

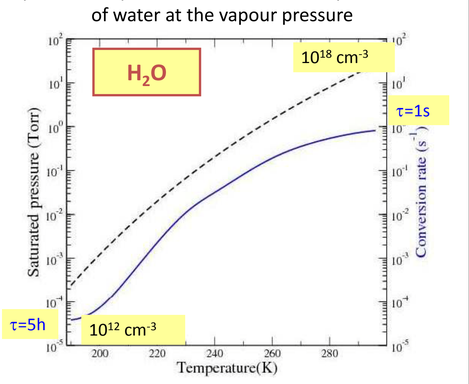
H_2CO



Tudorie *et al* A&A 453 (2006)

CALCULATIONS

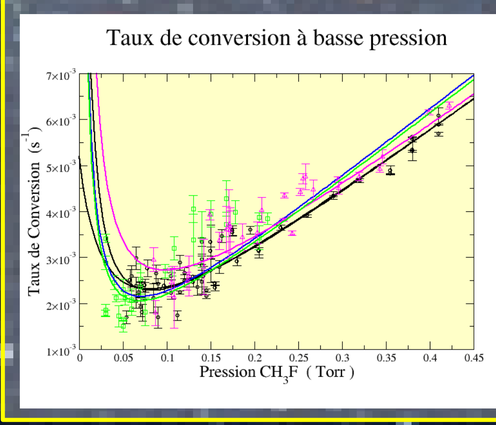
Temperature dependence of the nuclear spin conversion of water at the vapour pressure



Cacciani *et al* PRA 80 (2009), PRA 85 (2012)

Calculations performed extrapolated to the case of water embedded in rare gas solid at 4.2 K are coherent with conversion time of about 10 h observed experimentally in dilute samples.
Magnetic intermolecular interactions that explain acceleration of the NSC in concentrated rare gas solid has to be implemented for the gas phase.

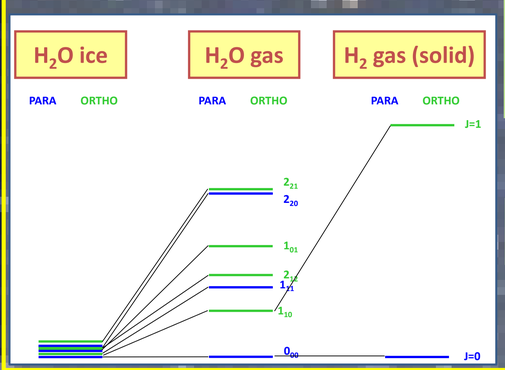
Calculations taking into account magnetic intramolecular interactions and collisional induced energy relaxation show that Nuclear Spin Conversion is very dependent on the the density and temperature of the gas phase.



EXPERIMENTAL

While the presence of electric fields in the vicinity of the molecule has been shown to accelerate nuclear spin conversion for CH_3F (Tudorie et al Surf. Science (2007), Cacciani et al J. Mol. Spec. 780 (2006)), we did not observe nuclear spin disequilibrium in the gas phase at low temperature (typ. 40-50 K) for CH_4 (Cermak et al , J. Mol Spec. 2012).

5. Conclusions and Perspectives : GAS-SOLID interface



For H_2 trapped on Amorphous Solid Water (Chehrouri et al PCCP 13 (2011)), it was shown that without the presence of magnetic impurities the nuclear spin conversion in slow (τ>4h) at low temperature. Thermal desorption does not induce important NSC in contrary of what it is observed for rotating molecules in rare gas solids.

The difference between the rotational energetic structures and the low ability of the icy surface to absorb the released energy may be crucial.

In the meanwhile, thermal desorption experiments for water from ASW (Hama et al ApJL 2011) have shown that high temperature OPR value is obtained since 150 K.

Disequilibria observed in space may be due to interactions in a mixture of solid and gas or due to the effects induced by UV or IR radiations. Development are in progress in LPMAA-Paris, PhLAM-Lille and PIIM-Marseille to answer this question.