SF2A 2008
C. Charbonnel, F. Combes and R. Samadi (eds)

SPECTROSCOPY AND NUCLEAR SPIN CONVERSION OF A MOLECULE OF ASTROPHYSICAL INTEREST IN RARE GAS MATRICES : METHANE

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Abstract. Many hydrogenated species observed in space in cold media, exist in different nuclear spin configurations. In cometary's atmospheres and in interstellar molecular clouds, the relative populations of these 'nuclear spin isomers' deviate significantly from the thermal equilibrium. Experimental studies are therefore required to understand the parameters governing the nuclear spin enrichment and conversion in astrophysical conditions, especially in presence of ice. We present new experimental results of the nuclear spin conversion dynamics for CH_4 trapped in rare gas matrices between 4K and 20K. Results revealed for methane are compared to those obtained with water.

1 Introduction

Methane and other hydrogenated molecules of astrophysical interest like H_2, H_2O, H_2CO, NH_3, CH_3OH, or C_2H_4 play an important role for the chemistry in the interstellar medium (ISM) and in the protosolar nebula. Because of the spin 1/2 of the protons, these molecules exist in different nuclear spin configurations. In case of four protons as it is for methane, they are called *ortho*, *para* and *meta* isotopomers depending whether the total nuclear spins are *I=1*, *I=0* or *I=2*, respectively. Due to the Pauli's exclusion principle and the properties of symmetry of rovibrational and spin wave functions of the molecule, each species can be identified by its own rotation-vibration spectrum. In the high temperature limit ($> 50\ K$), it is known that 9/16 of the molecules are *ortho*, 5/16 are *meta* while 2/16 are *para*. Below 50 K, the E/A and F/A ratios become strongly temperature dependent. From these ratios of molecules measured in cometary *comae* (Crovisier 2006; Kawakita *et al* 2006) or in dark clouds (Dickens & Irvine 1999), it is expected to determine the formation conditions of molecules in space, and especially the formation temperature. However, very few experimental data are available concerning nuclear spin conversion in relevant astrophysical conditions.

2 Results and discussion

As a first step before studying ices of astrophysical interest, we have investigated the parameters involved in the nuclear spin conversion of methane isolated in rare gas matrices at low temperatures (between 4.5 K and 20 K). In these environments, the hydrogenated molecule vibrates and rotates almost freely within the cage made of rare gas atoms (Michaut 2004). The rovibrational spectra were recorded in the wavenumber range of 400-4000 cm^{-1} with a resolution of 0.15 cm^{-1} using a Bruker 113V FTIR spectrometer. After a fast cooling from 20 K to 4.2 K, populations of the nuclear spin species do not follow the Boltzmann distribution due to slow nuclear spin conversion. By following the time evolution of the transitions associated with each nuclear spin species, we have measured conversion times in various conditions. At 4.2 K, due to the presence of CH_4 as impurity, argon matrices can be stabilized in *Face Centered Cubic (FCC)* or *Hexagonal Close-Packed (HCP)* crystalline structures. We observed that the nuclear spin conversion is four times faster in the *HCP* structure than in the *CFC* one while the dimensions of the cage are similar in both cases. The strong acceleration of the nuclear spin conversion observed in case of water as the concentration of molecules increases in the sample is

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less important for methane (cf figure 1). The calculations performed by our group in the case of H_2O showed that intermolecular magnetic interactions are responsible for this concentration dependence. It seems then that $CH_4 - CH_4$ magnetic interactions are less efficient than for $H_2O - H_2O$ pairs. To confirm this fact, calculations are in progress in our group. For more diluted samples, we measured a characteristic times (100-700 minutes) depending of the molecule, the nature of the rare gas atom and the symmetry of the cage. It is then surprising that characteristic times in cryogenic matrices are much shorter than months estimated in ice (Tikhonov & Volkov 2002) at 77 K. These data strongly suggest that the environment of the molecule plays a crucial role on the nuclear spin conversion of hydrogenated molecules.

3 Conclusions

To conclude, we showed that nuclear spin conversion is very sensitive to intermolecular 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 different, preventing any direct extrapolation of theses results to the astrophysical context. Efforts are made by our group to experimentally investigate NSC in ice.

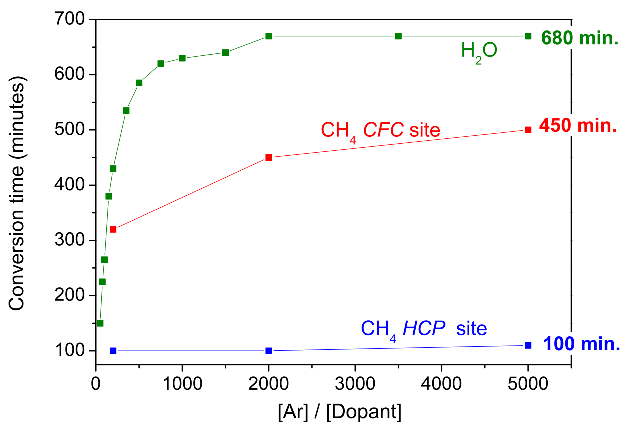

Fig. 1. Evolution of the nuclear spin conversion time of H_2O and CH_4 isolated in solid Ar in function of the dilution of dopant ([Rare Gas]/[Molecule]) at 4.2 K. On the right side of the figure are indicated the conversion times measured in the most diluted samples

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