SF2A 2009
M. Heydari-Malayeri, C. Reylé and R. Samadi (eds)

EQUILIBRATION OF NUCLEAR SPIN STATES OF CH_4 AT LOW TEMPERATURES

Lekic, A.[1], Michaut, X.[1], Bertin, M.[1], Fillion, J.-H.[1], Pardanaud, C.[2], Martin, C.[2] and Coussan, S.[2]

Abstract. Hydrogenated molecules are observed in astrophysical cold media as interstellar media (ISM) or cometary atmospheres. In many cases, the relative populations of each nuclear spin configuration of these hydrogenated species diverge strongly from their value at thermal equilibrium in the gaseous phase. In order to understand the parameters ruling the nuclear spin states equilibration of these kind of molecules in astrophysical conditions, experimental studies are performed in cold media (solid and at gas-solid interface). We present the latest experimental results of NSC dynamics for methane trapped in argon matrix between 4.3 K and 20 K. Preliminary results concerning nuclear spin states equilibration in a cold closed cell are also presented.

1 Introduction

CH_4 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 *nebulae*. Because of the spin 1/2 of the protons, these molecules exist in different nuclear spin configurations. The four protons of methane gives three nuclear spin modifications called *para*, *ortho*, and *meta* depending whether the total nuclear spins are $I = 0$, $I = 1$, or $I = 2$, respectively. Due to the Pauli's exclusion principle and the symmetry properties of the rovibrational molecular wave functions, each species *para*, *ortho*, and *meta* is associated to species E, F, and A of the T_d point group respectively. Each nuclear spin modification can be identified by its rotation-vibration spectrum. In the high temperature limit ($> 50K$) and thermodynamical equilibrium, it is known that 13 % of the molecules are *para*, 56 % are *ortho* while 31 % are *meta*. 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 laboratory studies are available concerning nuclear spin conversion in relevant astrophysical conditions. We present here a study of the nuclear spin equilibration at low temperature using the mid-infrared spectroscopy of CH_4 in argon matrix and at gas-solid interface. The spectra were recorded in the frequency range 400-4000 cm^{-1} with medium resolutions using FTIR spectrometers.

2 Nuclear Spin Conversion in rare gas matrix

First, we have investigated the parameters involved in the nuclear spin conversion of methane isolated in argon matrix at low temperatures (between 4.3 and 20 K). In this kind of environment, the hydrogenated molecules vibrate and rotate almost freely within the cage made of rare gas atoms (Michaut 2004). After a fast cooling from 20 K to 4.3 K, populations of the nuclear spin species do not follow a Boltzmann distribution because of a slow nuclear spin conversion. Following the time evolution of the transitions associated with one or the other species, we have measured characteristic times of nuclear spin conversion in various conditions. We observed that rare gas can be stabilized in Face-Centered Cubic (FCC) or Hexagonal Close-Packed (HCP) crystal structures for which the measured conversion times (450 minutes in FCC and 100 minutes in HCP) are clearly different,

[1] Laboratoire de Physique Moléculaire pour l'Atmosphère et l'Astrophysique-UMR CNRS 7092, Université Paris 6, 4 place Jussieu, 75252 Paris cedex 5

[2] Laboratoire Physique des Interactions Ioniques et Moléculaires - UMR CNRS 6633 - Université de Provence - Centre Saint-Jérôme - 13397 Marseille Cedex 20

despite the fact that both cages have similar dimensions. We observed that the NSC rate constant increases concomitantly with respect to the methane concentration in argon matrix. This phenomenon can be compared to the strong acceleration of the NSC of water in rare gas matrices as the concentration increases (Pardanaud 2008). Numerical calculations showed that the intermolecular magnetic interactions are responsible for this concentration dependence.

3 Nuclear spin equilibration at gas-solide interface

IR-driven experiments have been performed in pure gas or in gas-solid mixture in a closed cell under various pressure and temperature conditions above 55 K . Figure 1 shows that infrared spectrum of gaseous methane in the ν_3 stretching mode region is affected by the presence of solid methane in the cell. This effect is illustrated on Figure 1.b. In case of the R(1) line corresponding to the F species, the relative intensity decreases by 30 % in presence of solid methane. Further experimental developments are in progress to confirm this effect at lower temperature with a better signal-to-noise ratio and a good sensitivity.

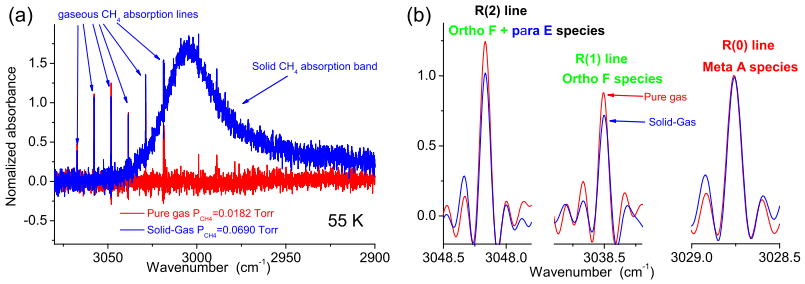

Fig. 1. FTIR spectra in the region of the stretching vibrational mode ν_3 of CH_4 obtained in pure gas and in solid-gas mixture obtained at 55 K. (a) whole spectrum and (b) zoom on the rovibrational lines R(0), R(1) et R(2) of the molecules in the gaseous phase

4 Conclusions

The environment of the molecule seems to play a crucial role on the nuclear spin conversion of hydrogenated molecules as it has already been pointed out for water embedded in different rare gas matrices (Pardanaud 2008, Abouaf-Marguin 2009). Due to the sensitivity of the Nuclear Spin Conversion to the intermolecular magnetic interactions, the decrease of mean distance between methane molecules enhances the NSC of methane trapped in rare gas solid. This process might be faster in solid methane (or solid ice in general). Furthermore, as rotation of molecules in ice is blocked, the mechanism for the dissipation of the rotational energy might be different. Extrapolation to the astrophysical context is not straight forward. In the meanwhile, efforts are made to investigate the possible influence of the solid methane on the equilibration of the nuclear spin states at low temperature.

This work has been performed within the project entitled CoSpiNu which was financially supported by INSU through the national programs 'Planétologie' and 'Physique et Chimie du Milieu Interstellaire'

References

Abouaf-Marguin, L., Vasserot, A.-M., Pardanaud, C.,& Michaut X. 2009, Chem. Phys. Lett. 480, 82

Crovisier, J. 2006, Molecular Physics 104, 2737

Dickens,J. E. & Irvine,W. M. 1999, ApJ 518, 733

Kawakita, H., Dello Russo, N., Furusho, R., *et al* 2006, ApJ 643, 1337

Michaut, X., Vasserot, A.-M., & Abouaf-Marguin, L. 2004, Vib. Spectrosc. 34, 83

Pardanaud, C., Michaut,X., Fillion, J.-H., Vasserot, A.-M., & Abouaf-Marguin, *in* Journées de la SF2A 2008, eds. C. Charbonnel, F. Combes, & R. Samadi (Paris, 2008), 337, 2008