

Report from the Workshop on Nuclear Spin Effects in Astrochemistry

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1 Introduction

In recent years, detailed experimental and theoretical work on low-temperature chemical reactions has highlighted the relevance of nuclear spin specific investigations in astrochemistry. This has prompted the inclusion of nuclear spin dependent reaction rates in theoretical models of interstellar chemistry - unveiling some dramatic effects for example on isotope fractionation [1]. At the same time, the amount of observational data on nuclear spin ratios in astronomical environments has grown rapidly. Measurements of ortho-to-para ratios (OPRs) in comets are thus getting more systematic while those in the interstellar medium (ISM) have been accumulating. In general, the interpretation of these measurements is difficult and often controversial. The second workshop "Nuclear Spin Effects in Astrochemistry" was held in Grenoble, France, May 2-4, 2017. Following the success of the first edition (held in Göteborg in 2014), the aim of this second workshop was again to bring together experts from both the experimental, theoretical and observational communities to present and discuss the current status and the new challenges of interpreting the growing amount of data on molecular spin ratios. The scientific program consisted of invited talks, contributed talks, as well as four 30-minutes sessions of discussion. A short summary of the presentations is given below.

2 Summary of talks

2.1 Observations

Observationally, a review of the Herschel measurements of the water OPRs in the ISM was given by D. Lis. These OPRs are in most cases consistent with the high-temperature limit of 3 but several low values (down to 0.1) have been also reported. These results are however model dependent and a close re-examination now suggests values consistent with ~ 3 given the large uncertainties [2]. The observations of H_2Cl^+ in the diffuse ISM have been reviewed by D. Neufeld. The measured OPRs are consistent with the high-temperature limit of 3 within the observational error bars, which provides strong constraints on the H_2Cl^+ nuclear spin chemistry [3]. In contrast, the OPR of H_3^+ in diffuse clouds varies between 0.4 and the high-temperature limit of 1, as presented by K. Crabtree. The spin temperature of H_3^+ is also systematically below that of H_2 [4] (see below). In the dense ISM, the OPRs of the deuterated isotopologues of H_3^+ and NH_3 have been measured with the APEX and SOFIA telescopes (see below). The OPR of water in comets was reviewed by B. Bonev and G. Villanueva. They discussed how current measurements are biased toward a spin temperature of ~ 30 K (OPR=2.5) due to the under-reporting of high water OPRs. Preliminary results based on new methodologies give a median OPR of 2.9 [5]. A survey of the OPR of NH_2 in comets was also presented by H. Kawakita. The observed values are found to cluster around 3.2 (i.e. 1.1 for NH_3), suggesting here again a spin temperature of ~ 30 K [6]. The need

for systematic studies (many comets/molecules) was emphasized and future studies should investigate both hydrides (NH_3 and CH_4) and organics (H_2CO , C_2H_6 and CH_3OH).

2.2 Experiments

Experimentally, progress toward understanding the mechanisms controlling the OPR of H_2O in the ISM was reviewed by T. Hama. The OPRs of H_2O desorbed from water ice at 10 K have been measured and found to be equal to the statistical high-temperature OPR of 3, invalidating the usually assumed relation between OPR and temperature [7]. Adsorption and ortho/para conversion was also studied for H_2 chemisorbed on a Pd(210) surface at 30 K, as presented by K. Fukutani. The adsorption energy of ortho- $\text{H}_2(j=1)$ was found to be larger than that of para- $\text{H}_2(j=0)$ by about 100 K, and the ortho/para conversion was shown to be rapid (~ 1 s) and much faster than for physisorbed H_2 [8]. Nuclear spin conversion of H_2 , CH_4 and H_2O was also studied in rare gas matrices, as discussed by X. Michaut. Characteristic times were found to vary from a few minutes to several hours (in the range 4-30 K) and extrapolation to pure ice suggests a very rapid nuclear spin conversion in icy mantles [9]. In the gas-phase, a new efficient method (“magnetic focussing” in a supersonic beam) to prepare water enriched in the ortho form (up to an OPR of 20) was presented by P. Ayotte. Interconversion kinetics of the stored enriched water was investigated in rare gas matrices and it has revealed strong temperature and isotope (^{17}O and ^{18}O) effects [10]. The evolution of the OPR of water vapor was also recently studied in a supersonic expansion, as presented by R. Georges. Despite the presence of water clusters in the jet, no interconversion was observed in this experiment [11], in contrast to the results of [12]. Finally, cryogenic ion trap experiments were presented by D. Gerlich. Among recent results, the spectroscopic characterization of the He-H_3^+ system has been achieved [13], thus enabling future searches for the ortho and para He-H_3^+ complexes in the cold ISM.

2.3 Theory

Theoretically, a new method to derive nuclear spin selection rules for reactive collisions was presented by H. Schmiedt. It allows to unify the approaches of Quack [14] (permutation symmetry) and Oka [15] (rotational symmetry) and it is particularly well adapted for the description of molecules that are large and/or contain nuclei with spins $I > 1/2$ [16]. Dynamical calculations, based on global potential energy surfaces (PES), were also described for the ortho/para conversion of H_2 and H_3^+ . Both exact and statistical quantum mechanical calculations were presented by T. Gonzalez-Lezana for the (thermoneutral) reaction $\text{H}_2 + \text{H}^+$. The statistical approach was shown to be accurate for this complex-forming reactions [17]. A dynamically biased statistical model based on quasi-classical trajectories (QCT) was presented by O. Roncero for the five-proton reaction $\text{H}_3^+ + \text{H}_2$. This model is able to reproduce the evolution of the reaction from statistical at low temperature (< 200 K) to a direct hop mechanism above room temperature [18]. Calculations are in progress in the group of O. Roncero for the $\text{H}_3^+ + \text{H}$ reaction, of interest for the diffuse interstellar medium.

2.4 Models

Finally, several models of spin-state chemistry were presented. They nowadays contain a consistent description of symmetry rules within the full scrambling hypothesis, as presented by O. Sipilä. Recently his group has been able to reproduce SOFIA and APEX observations of the para and ortho forms of both H_2D^+ and D_2H^+ toward a protostar, suggesting an age of $\sim 5 \times 10^5$ yr for the core and twice this age for the ambient cloud [19]. This group has also investigated the ammonia deuterated isotopologues but their current model fails to reproduce the observed OPRs, suggesting either a breakdown of the full scrambling hypothesis or a contribution of grain surface chemistry, as discussed by J. Harju [20]. P. Hily-Blant presented a similar model where the OPRs of the H_3^+ isotopologues were shown to be entirely driven by H_2 and to be at steady-state in prestellar cores [21]. The spin chemistry of H_3^+ in the diffuse ISM was discussed by K. Crabtree. He has shown that the excess of para- H_3^+ cannot be explained by

the latest experiments and models. A possible solution could be found in the temperature variations in diffuse clouds, as being explored by D. Neufeld. R. Le Gal presented new results on the spin-state chemistry of NH_2 and H_2Cl^+ . The thermalization reaction of NH_2 by H was found to be rapid while energy barriers were found in both $\text{H}_2\text{Cl}^+ + \text{H}$ and $\text{H}_2\text{Cl}^+ + \text{H}_2$, questioning the use of the full scrambling hypothesis [22]. Finally, the role of dust grains in the ortho/para conversion of H_2 has been studied by E. Bron using a statistical formalism for the description of the grain temperature fluctuations. This model is able to reproduce the H_2 OPRs observed in photo-dissociation regions (PDRs)[23].

3 Conclusions and perspectives

All the above advances promise a bright future for nuclear spin astrochemistry. Among many perspectives, accurate estimates of the uncertainties on the observational OPRs is seen as a priority, both for the ISM and for comets. This is necessary for a meaningful interpretation of the “spin” temperatures and of their potential spatial variations. OPR measurements of daughter molecules (e.g. H_2O^+ for H_2O) and organic species (e.g. C_2H_6) is another important observational issue. Experimentally, the interconversion kinetics, both in the gas and solid phases, is still an open question despite significant progress. The new enrichment methodologies for the preparation of out-of-equilibrium spin populations will enable studies of interconversion mechanisms and rates. For the gas-phase, cryogenic traps offer ideal environments to probe and manipulate individual states of molecules in proton/deuteron scrambling reactions, e.g. for the key reaction $\text{H}_3^+ + \text{H}_2$. Nuclear spin conservation in photodissociation reactions (e.g. $\text{NH}_3 + \text{photon} \rightarrow \text{NH}_2 + \text{H}$) should also be investigated in the laboratory. Theoretically, a quantum statistical approach for systems with more than 3 atoms need to be developed in order to predict nuclear spin branching ratios in thermoneutral complex-forming reaction. As an alternative, the ring polymer molecular dynamics (RPMD) method seems like a promising tool to include quantum effects in reactions involving many identical particles. Finally, the new generation of chemical models including spin-state chemistry will provide crucial constraints to identify the dominant interconversion reactions and to quantify the competition between gas-phase and solid-phase nuclear spin processes in astronomical environments.

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