

Nuclear spin effects in astrochemistry

2-4 May 2017
Grenoble

France

Table of contents

Nuclear spin states in molecules: Unified rotational and permutational symmetry and selection rules in reactive collisions, Hanno Schmiedt [et al.]	4
Spin dynamics of water ice and ortho-to-para ratio of gaseous water desorbed from ice, Tetsuya Hama [et al.]	6
Preparation, characterization and storage of water vapours highly enriched in its ortho-H ₂ O nuclear spin isomer, P.-A. Turgeon [et al.]	8
Nuclear spin symmetry conservation in H ₂ O investigated by direct absorption FTIR spectroscopy of water vapor cooled down in supersonic expansion, Robert Georges [et al.]	10
The Ortho-to-Para Ratio in Interstellar Water, Darek Lis	12
Spin ratios in comets: complexity of measurements, post-2014 updates, and prospects, Boncho Bonev	14
Nuclear spin restrictions in gas phase reactions: more experiments are needed!, Dieter Gerlich	16
Steady-state nuclear spin chemistry in dark clouds, Pierre Hily-Blant	18
Ortho-para transitions of molecular hydrogen in H ⁺ + H ₂ collisions, Tomas Gonzalez-Lezana [et al.]	20
Rotational state and ortho-para conversion of H ₂ on solid surfaces, Katsuyuki Fukutani	22
H ₂ ortho-para ratio : the role of dust grains, Emeric Bron [et al.]	24
Ortho/para conversion of H ₃ ⁺ in collisions with H ₂ and H, Octavio Roncero	26
The ortho:para ratio of the trihydrogen cation in diffuse molecular clouds, Kyle Crabtree	28

What do we know about time scales for the nuclear spin conversion in molecular ices and at the solid-gas interface?, Xavier Michaut [et al.]	30
Spin states of H_2D^+ and D_2H^+ as chemical age tracers, Olli Sipilä	32
Do spin temperatures differ between molecules in comets? The case for H_2O , CH_4 , NH_3 , C_2H_6 and CH_3OH , Geronimo Villanueva	34
Spin-state chemistry of deuterated ammonia, Jorma Harju [et al.]	36
Nuclear Spin Isomers in Cometary Molecules: Survey for Ortho-to-Para Ratios of Ammonia in Comets, Hideyo Kawakita [et al.]	38
Spin Effects in Molecular Clouds, Steven Charnley	40
Ortho-to-para ratios as powerful interstellar diagnostics, Romane Le Gal [et al.]	42
The ortho-to-para ratios measured for triatomic hydrides in the diffuse interstellar medium, David Neufeld	44
List of participants	45
List of sponsors	47

Nuclear spin states in molecules: Unified rotational and permutational symmetry and selection rules in reactive collisions

Hanno Schmiedt ^{*† 1}, Stephan Schlemmer ², Per Jensen ³

¹ I. Physikalisches Institut, Universität zu Köln – Zùlpicher Strasse 77, D-50937 Köln, Germany, Germany

² I. Physikalisches Institut, Universität zu Köln – Germany

³ Bergische Universität Wuppertal – Universität Wuppertal Gaußstraße 20 42119 Wuppertal Postfach: 42097 Wuppertal Phone: +49 202 439-0 E-Mail: webmaster@uni-wuppertal.de Internet: www.uni-wuppertal.de, Germany

The symmetry of a system wave function is one of the cornerstones of modern physics and chemistry. In particular, symmetry-based selection rules for reactive molecular collisions are important prerequisites for studying intermolecular dynamics. Focusing on the nuclear spin states of molecules, two main symmetry groups can be identified: The individual spin symmetry, conventionally interpreted as of rotational nature, and the permutation symmetry for identical nuclei. In the first part of this talk, a general tool to coherently determine the symmetry of the molecular wave function in both symmetry groups is introduced. This includes the formulation of a one-to-one correspondence between a total nuclear spin quantum number and the exchange symmetry of the nuclei. In the second part, the main focus is on reactive collisions, where the symmetry of the intermediately formed complex is shown to strongly inhibit or facilitate, e.g., spin-flip transitions. This symmetry is determined by the potential energy surface of the intermediate complex. Although this depends on energy, no other dynamical effects are included explicitly. In conclusion, the talk will show a rather simple but elegant way to find selection rules for reactive collisions in particular if the intermediate symmetry group is restricted by potential energy barriers.

*Speaker

†Corresponding author: schmiedt@ph1.uni-koeln.de

Notes

Spin dynamics of water ice and ortho-to-para ratio of gaseous water desorbed from ice

Tetsuya Hama * ¹, Akira Kouchi ¹, Naoki Watanabe ¹

¹ Institute of Low Temperature Science, Hokkaido University – Japan

A key observable related to interstellar water chemistry is the abundance ratio of nuclear spin isomers (the ortho-to-para ratio, OPR), because it can be a tracer of the physical and chemical history of H₂O. Cometary comae, and star- and planet-forming regions have OPRs for H₂O (0.1–2.4), which are anomalously lower than the statistical value of 3. These observed OPR values have been used to probe the formation temperature of water ice on interstellar dust. However, the use of the OPR as a probe requires the assumption that the OPR of H₂O desorbed from ice is related to the ice temperature. However, the OPR of H₂O desorbed from ice remains poorly understood, and the above assumption has not been validated. Thus, the significance of the OPR of interstellar water is still unknown.

We review recent experimental progress towards understanding the mechanisms controlling the OPR of interstellar H₂O. For example, we performed direct measurements of the OPR of water desorbed from water ice at 10 K. The desorbed water showed the statistical high-temperature OPR of 3; the OPR did not reflect the formation temperature of the ice (10 K, OPR = 0.3). This invalidates the assumed conventional relation between OPR and temperature. Reinterpretation of its importance by considering gas-phase processes may clarify new or missed roles of interstellar H₂O in star and planet formation. We speculate that it may be an indicator of the gas-phase nuclear-spin conversion processes that the H₂O experienced (e.g., reactions with H⁺ and H₃O⁺).

Hama, T., Watanabe, N., *Chem. Rev.*, 2013, 113, 8783.

Hama, T., Kouchi, A., Watanabe, N., *Science*, 2016, 351, 65.

Gerlich, D., Windisch, F., Hlavenka, P., Plasil, R., Glosik, J., *Phil. Trans. R. Soc. London A*, 2006, 364, 3007.

Lique, F., Honvault, P., Faure, A., *Int. Rev. Phys. Chem.*, 2014. 33, 125.

*Speaker

Notes

Preparation, characterization and storage of water vapours highly enriched in its ortho-H₂O nuclear spin isomer

P.-A. Turgeon ¹, J. Vermette ¹, G. Alexandrowicz ², Y. Peperstraete ³, L. Philippe ³, M. Bertin ⁴, J.-H. Fillion ⁵, X. Michaut ⁵, Patrick Ayotte * ⁶

¹ Université de Sherbrooke – Canada

² Technion - Israel Institute of Technology – Israel

³ LERMA, Observatoire de Paris, PSL Research University, CNRS, Sorbonne Universités, UPMC Univ. Paris 06 – 2LERMA, Observatoire de Paris, PSL Research University, CNRS, Sorbonne Universités, UPMC Univ. Paris 06 – France

⁴ LERMA, Observatoire de Paris, PSL Research University, CNRS, Sorbonne Universités, UPMC Univ. Paris 06 – United States

⁵ LERMA, Observatoire de Paris, PSL Research University, CNRS, Sorbonne Universités, UPMC Univ. Paris 06 – Université Pierre et Marie Curie - Paris 6 – France

⁶ Université de Sherbrooke – Département de chimie Université de Sherbrooke 2500 boulevard université Sherbrooke, Québec CANADA J1K 2R1, Canada

The properties and behaviour of the nuclear spin isomers (NSI) of the water molecule are of great interest in astrophysics since the ortho:para ratio (OPR) is assumed to provide insight into the formation mechanism and history of comets [1] as well as other celestial bodies [2]. Technological advances are also foreseen for ortho-H₂O enriched samples in magnetic resonance applications, by analogy with hyperpolarisation experiments using para-hydrogen. Motivated by these perspectives, methodological bottlenecks need to be overcome: 1-the development of efficient separation protocols, and 2-the improvement in storage strategies for water sample enriched in either of its NSI through a better understanding of their inter-conversion mechanism. We will show how magnetic focussing in a supersonic molecular beam [3] provides a convenient method for preparing water vapour strongly enriched (i.e., > 15:1) in the ortho-H₂O NSI. We will also show that rare gas matrices can be an efficient condensed phase storage medium for enriched samples [4] whose lifetime remains however, limited by the slow interconversion kinetics of NSI causing sample enrichments to decay over several hours. Closer examination of the NSI inter-conversion kinetics of isolated water molecules, trapped in rare gas matrices, revealed that it increases significantly in the heavy water isotopologues H₂¹⁷O and H₂¹⁸O compared to normal water, and that it increases rapidly above T~10K.[5] The temperature and isotope effects may provide valuable insight into the interconversion mechanism and, in particular, the role of confinement on the intramolecular couplings (i.e., spin-rotation and spin-spin) responsible for the inter-conversion between the ortho and para NSI of the water molecule. Finally, perspectives for the application of ortho-H₂O to study chemical dynamics at ice surfaces will be discussed.

1. Crovisier, J., et al., Science **275**, 1904-1907 (1997); Mumma, M.J. et al., Science **232**, 1523-1528 (1986);

*Speaker

2. Hogerheijde, M.R., et al., *Science* **334**, 338-340 (2011);
3. Kravchuk et al., *Science* **331**, 319-321 (2011);
4. Turgeon et al., *Phys.Rev.A* **86**, 062710 (2012).
5. Turgeon, P.-A., et al, accepted for publication in *J. Phys. Chem. A*.

Notes

Nuclear spin symmetry conservation in H₂O investigated by direct absorption FTIR spectroscopy of water vapor cooled down in supersonic expansion

Robert Georges ^{*†} ¹, Xavier Michaut[‡], Audrey Moudens, Manuel Goubet, Olivier Pirali, Pascale Soulard, Pierre Asselin, Thérèse Huet, Pascale Roy, Martin Fournier, Andrey Vigasin[§]

¹ Institut de Physique de Rennes (IPR) – Université de Rennes 1, CNRS : UMR6251 – Bâtiment 11A
F-35042 Rennes, France

We report the results of an experimental study related to the relaxation of the nuclear spin isomers of the water molecule in a supersonic expansion. Rovibrational lines of both ortho- and para- spin isomers were recorded in the spectral range of H₂O stretching vibrations using FTIR direct absorption. Water vapor seeded either in argon, helium or oxygen (or in a mixture of oxygen with argon) was expanded into vacuum through a slit nozzle. Partial water vapor pressure in the mixture varied in a wide range from 1.5 to 110.0 hPa. Depending on expansion condition, the effect of water vapor aggregation was clearly seen in some of our measured spectra. The Boltzmann-plot examination of the lines intensities made possible the determination of the H₂O rotational temperatures in the isentropic core and in the lateral shear layer probed zones of the planar expansion. The study of the OPR, i.e the ratio of the ortho- to para- absorption line intensities as a function of T_{rot} , did not reveal any signs of the OPR relaxed to the sample temperature. In contrast, the OPR was always conserved in agreement with the stagnation reservoir equilibrium temperature. This result differs from that of a previous study carried out under similar conditions [Manca Tanner et al. J. Phys. Chem. A 2013, 117, 10105–10118]. The conservation of the OPR was found irrespective of whether water molecules aggregation was pronounced or not. Also no effect of the paramagnetic oxygen admixture on enhancing the OPR relaxation was observed.

*Speaker

†Corresponding author: robert.georges@univ-rennes1.fr

‡Corresponding author: xavier.michaut@upmc.fr

§Corresponding author: avigasi@rambler.ru

Notes

The Ortho-to-Para Ratio in Interstellar Water

Darek Lis * ¹

¹ LERMA, Observatoire de Paris – LERMA, Observatoire de Paris – 61, avenue de l’Observatoire, 75014 Paris, France

The ortho-to-para ratio in water has been suggested to be of interest for understanding the formation and the thermal history of water ices in the interstellar medium and protoplanetary disk environments. I review Herschel measurements of the water ortho-to-para ratio, which in most cases are consistent with the high-temperature LTE limit. Several lower values have also been reported, but their implications remain unclear, accentuating the need for new laboratory measurements involving water freeze-out and evaporation processes under low-temperature conditions, similar to those present in the interstellar medium.

*Speaker

Notes

Spin ratios in comets: complexity of measurements, post-2014 updates, and prospects

Boncho Bonev * ¹

¹ American University (AU) – 4400 Massachusetts Ave NW, Washington, DC 20016, United States

Spin ratios measured in comets are often cross-referenced between astronomical and chemical physics journals. This workshop is an excellent venue to bridge the two communities and discuss not only bottom line results (easily accessible in review articles), but also caveats behind these remote sensing measurements that need to be taken into account when placed in context of theoretical and experimental work. This presentation will therefore outline why obtaining accurate spin ratios in comets is a feasible, but also quite a challenging task. The talk will highlight (1) factors contributing to improved accuracy of measurements, and (2) possible (and often overlooked) measurement biases, which need to be taken into account when comet spin ratios are communicated to other fields of research. This talk will then outline ongoing work since the first workshop edition in 2014 (Chalmers, Göteborg, Sweden) to overcome these limitations, in particular, retrievals of spin ratio for H₂CO at infrared wavelengths in comet C/2002 T7 (LINEAR) from archival data. We will also highlight H₂O spectra of comet 45P/Honda-Mrkos-Pajdusakova from a newly commissioned (fall of 2016) high-resolution spectrograph (iSHELL) at the NASA Infrared Telescope Facility. The large free spectral range and sensitivity of iSHELL will likely make it a premium instrument for obtaining spin ratios (and rotational excitation temperatures) in comets.

*Speaker

Notes

Nuclear spin restrictions in gas phase reactions: more experiments are needed!

Dieter Gerlich * ¹

¹ Technische Universität Chemnitz (TUC) – 09126 Chemnitz, Germany

Three years ago I summarized in Göteborg the progress made in *Experimental search for nuclear spin restrictions* and I closed with an optimistic outlook announcing measurements for state changing $\text{H}_3^+(J_G) + \text{H}_2(J)$ collisions and low temperature rate coefficients for ortho-para transition in slow collisions of $\text{H}_2(J=1)$ with protons. The technical tools (predominantly cryogenic ion traps) are available since many years; however, unfortunately, progress is very slow. Therefore I first recapitulate in my introduction some *ancient* experiments and their interpretations with a simple statistical model. This model is based on the sound assumption that (i) collision complexes are formed with the statistical weight of the total nuclear spin, $2I + 1$, and that (ii) I is conserved in the (statistical?) decay towards reactants or products.

In a short experimental section I mention the typical parts of cryogenic trap apparati as they have been used in Prague, Basel, and Köln for studying $\text{FeO}^+ + \text{H}_2$ [1] reactions, for confirming C_{60}^+ as a carrier of NIR DIB's [2], and for spectroscopy of He-H_3^+ [3], respectively. Central problems in experiments with para-hydrogen are the preparation of pure p- H_2 and the *in situ* detection of o- H_2 impurities. Of special interest (also for astrophysics and ice experiments) is the conversion of H_2 attached to the cold surfaces surrounding the trap. Very sensitive sensors for measuring the OPR are deuteration of trapped H_3^+ with traces of HD or NH^+ formation in collisions of N^+ with H_2 .

In the main part I will summarize our longstanding activities (in Köln) aiming to understand the “simple” system $\text{H}_3^+(J_G) + \text{H}_2(J)$. A significant step forward has been the new scheme to probe the population of trapped H_3^+ ions via LIICG (laser induced inhibition of complex growth). In contrast to laser induced reactions this method is non-destructive, the ions can be recycled. A high resolution IR laser allows us to characterize the states of He-H_3^+ [3]. A first attempt to distinguish between ortho and para complexes is mentioned. Finally I will discuss rate coefficients we measured recently for $\text{FeO}^+ + \text{n-H}_2$ [1]. The formation of $\text{Fe}^+ + \text{H}_2\text{O}$ shows an extremely steep temperature dependence and, for p- H_2 and o- H_2 , significant differences can be expected.

In the outlook I express (again) my hope that more experimental groups will apply and improve cryogenic traps to understand *Astrochemistry*. The methods are in our hands!

1. D. Gerlich, J. Jašík, E. Andris, R. Navrátil, J. Roithová, Collisions of FeO^+ with H_2 and He in a Cryogenic Ion Trap, *ChemPhysChem* 17 (2016) 3723
2. K. Campbell, M. Holz, D. Gerlich & J.P. Maier Laboratory confirmation of C_{60}^+ as carrier of two diffuse inter- stellar bands. *Nature* 523 (2015), 322
3. I. Savic, D. Gerlich, O. Asvany, P. Jusko, S. Schlemmer, Controlled synthesis and analysis of He-H_3^+ in a 3.7 K ion trap, *Molecular Physics*, 113 (2015) 2320

*Speaker

Notes

Steady-state nuclear spin chemistry in dark clouds

Pierre Hily-Blant * 1,2

¹ Institut de Planétologie et d'Astrophysique de Grenoble (IPAG) – OSUG, Université Joseph Fourier - Grenoble I, INSU, CNRS : UMR5274 – 414, Rue de la Piscine BP 53 38041 Grenoble Cedex 9, France

² Institut Universitaire de France (IUF) – Ministère de l'Enseignement Supérieur et de la Recherche Scientifique – Maison des Universités, 103 Boulevard Saint-Michel, 75005 Paris, France

The physical and chemical conditions prevailing in the densest parts of prestellar cores provide the initial conditions for the next phase of evolution during the star formation process, namely the protostar stage. However, observations of the inner regions of prestellar cores are challenged by the depletion of gas-phase species through freeze-out. Indeed, the complete depletion scenario of Walmsley et al. (2004) [1] suggests that all heavy molecules eventually disappear from the gas-phase, and observers would be left with D-isotopologues of H_3^+ . Regardless, among the few species observed in the densest parts of prestellar cores are hydrides having two or more H and/or D atoms for which the ortho-to-para ratios (OPRs) are required in order to derive their total abundances. Chemical models able to predict these OPRs are necessary. We here present an overview of the developments of nuclear spin chemistry in the context of prestellar cores. We will also present the nuclear spin network developed in our group in Grenoble, as well as preliminary results using a new version of our code where chemistry in a Larson-type collapse is solved self-consistently.

1. Walmsley et al., 2004, A&A, 418, 1035

*Speaker

Notes

Ortho-para transitions of molecular hydrogen in $\text{H}^+ + \text{H}_2$ collisions

Tomas Gonzalez-Lezana ^{*† 1}, Pascal Honvault ²

¹ Consejo Superior de Investigaciones Científicas (IFF-CSIC) – Serrano 123, 28006 Madrid, Spain

² Laboratoire Interdisciplinaire Carnot de Bourgogne (ICB) – CNRS : UMR6303, Université de Bourgogne – 9 avenue Alain Savary, BP 47870, 21078 Dijon Cedex, France

Due to their interest in an Astrophysical context [1,2] the rovibrational structure of H_2 and the ortho-para conversion during $\text{H}^+ + \text{H}_2$ reactive collisions have been studied in detail by means of an exact quantum mechanical (EQM) time independent approach [3] and a statistical quantum mechanical (SQM) method [4]. The comparison between both set of results allows to characterize the importance of complex-forming mechanisms in the overall dynamics of the process. Previous results for state-to-state rate constants between 10-100 K [5] have been recently completed to temperatures up to 3000 K [6].

1. L. Pagani, P. Lesaffre, E. Roueff, M. Jorfi, P. Honvault, T. González-Lezana, A. Faure, *Phil. Trans. R. Soc. A*, **370**, 5200 (2012)
2. L. Pagani, P. Lesaffre, M. Jorfi, P. Honvault, T. González-Lezana, A. Faure, *A&A*, **A38**, 551 (2013)
3. T. Rajagopala Rao, S. Mahapatra and P. Honvault, *J. Chem. Phys.* **141**, 064306 (2014)
4. T. González-Lezana, *Int. Rev. Phys. Chem.* **26**, 29 (2007)
5. P. Honvault, M. Jorfi, T. González-Lezana, A. Faure, L. Pagani, *Phys. Rev. Lett.* **107**, 023201 (2011); *Phys. Rev. Lett.* **108**, 109903 (2012)
6. T. González-Lezana and P. Honvault, *MNRAS*, **467**, 1294-1299 (2017)

*Speaker

†Corresponding author: t.gonzalez.lezana@csic.es

Notes

Rotational state and ortho-para conversion of H₂ on solid surfaces

Katsuyuki Fukutani * 1

¹ Institute of Industrial Science (IIS) – University of Tokyo, Tokyo 153-8505, Japan

The ortho-para (o-p) ratio of molecular hydrogen is of interest and importance in astrochemistry and physics. While the H₂ o-p conversion is forbidden in an isolated state, it is promoted when H₂ interacts with solid surfaces. The conversion time and residence time of H₂ on solid surfaces, therefore, are important parameters to understand the o-p ratio in space. In our previous studies, we have clarified the o-p conversion time during physisorption on a typical metal of Ag and amorphous ice surfaces to be ~ 600 and ~ 400 s, respectively [1]. Molecular hydrogen, on the other hand, is sometimes more strongly adsorbed on a surface, which may be called molecular chemisorption [2]. Due to the symmetry of the H₂ molecule, it is expected that the molecule-surface interaction is anisotropic depending on the molecular orientation modifying the rotational-energy state, which is also important for the o-p conversion [1,3]. In the present work, we have studied the adsorption and o-p conversion on such a molecular-chemisorption system of Pd(210) with rotational (J)-state selective temperature programmed desorption (TPD) and theoretical calculations [4].

When the Pd(210) surface is exposed to H₂ at ~ 30 K, H₂ is molecularly chemisorbed on a H-covered surface, which is revealed by a TPD peak at ~ 70 K [2]. When this desorption signal is J -state selectively detected, it is found that the $J=0$ para H₂ is desorbed at 74 K, while the $J=1$ ortho H₂ is desorbed at a higher temperature of 78 K. This indicates that the adsorption energy of the ortho species is larger than that of the para species. This is due to the lifting of the degeneracy of the ortho state induced by the potential anisotropy, and the adsorption energy difference is analyzed to be about 10 meV. It is noted that the population ratio of the ortho and para states does not change with time suggesting fast o-p conversion. If we plot the o-p desorption intensity ratio as a function of temperature, the ratio is found to deviate from the curve expected from the thermal equilibrium. With the aid of numerical simulations, the o-p conversion time is analyzed to be about 0.5 s. Furthermore, the o-p ratio in the adsorption state is estimated to be about 4 from the rotational energy state.

1. K. Fukutani, T. Sugimoto, Prog. Surf. Sci. 88, 279 (2013).
2. P. K. Schmidt et al., Phys. Rev. Lett. 24 87, 096103 (2001).
3. T. Sugimoto, K. Fukutani, Phys. Rev. Lett. 112, 146101 (2014).
4. S. Ohno, D. Ivanov, K. Fukutani, in prep.

*Speaker

Notes

H₂ ortho-para ratio : the role of dust grains

Emeric Bron ^{*† 1,2}, Franck Le Petit ³, Jacques Le Bourlot ^{2,4}

¹ Instituto de Ciencia de Materiales de Madrid [Madrid] (ICMM) – Sor Juana Inés de la Cruz, 3 28049 Madrid, Spain

² Laboratoire d’Etude du Rayonnement et de la Matière en Astrophysique (LERMA) – Université Pierre et Marie Curie [UPMC] - Paris VI, Observatoire de Paris, Université de Cergy Pontoise, Université Pierre et Marie Curie (UPMC) - Paris VI, INSU, CNRS : UMR8112, École normale supérieure [ENS] - Paris – 61, avenue de l’Observatoire - 75014 PARIS, France

³ LERMA (LERMA) – CNRS, CNRS : UMR8112 – France

⁴ Université Paris-Diderot (P7) – Ministère de l’Enseignement Supérieur et de la Recherche Scientifique – France

H₂ controls the transition to molecular gas and the subsequent development of chemical complexity, and is also a powerful diagnostics to study the radiative retroaction of stars on molecular clouds. Its ortho-para ratio affects the thermodynamical properties of the gas (equation of state, cooling) and controls several branches of the chemistry (nitrogen and deuterium chemistry). Yet, ISO and Spitzer observations of H₂ emission lines in Photo-Dissociation Regions (PDRs, edges of molecular clouds exposed to the radiation of massive stars) show ortho-para ratios consistently lower to what is expected at thermal equilibrium in this warm molecular medium [1], which remain unexplained.

Ortho-para conversion on the surface of dust grains is possible, and would tend to thermalize the ortho-para ratio to the dust temperature (lower than the gas temperature). However, this process is very sensitive to the dust temperature and can be suppressed by fast thermal desorption. Small grains account for most of the total dust surface, but undergo large temperature fluctuations caused by the absorption of UV photons. The statistical effect of these fluctuations needs to be taken into account.

I have thus developed a statistical formalism based on master equations to compute the average efficiency of surface ortho-para conversion perturbed by fluctuations of the grain temperature. Fluctuations are found to make ortho-para conversion efficient in PDR conditions, explaining quantitatively for the first time the observed ortho-para values [2]. In addition, temperature fluctuations make the efficiency of the conversion process much less sensitive to the microphysical uncertainties.

1. Habart, E., Abergel, A., Boulanger, F., Joblin, C., Verstraete, L., Compiègne, M., Pineau Des Forêts, G., and Le Bourlot, J., *A&A*, 527, A122 (2011)
2. Bron, E., Le Petit, F., and Le Bourlot, J. *A&A*, 588, A27 (2016)

*Speaker

†Corresponding author: emeric.bron@obspm.fr

Notes

Ortho/para conversion of H_3^+ in collisions with H_2 and H

Octavio Roncero * ¹

¹ Instituto de Física Fundamental, Consejo Superior de Investigaciones Científicas (IFF-CSIC) – Serrano, 123, 28006 Madrid, Spain

The ortho/para transformation of H_3^+ is mainly due to its collisions with H_2 . There are two reaction mechanisms, the proton hop and the exchange, and nuclear spin symmetry introduces differences among them. Thus experimental determination of the exchange/hop ratio has been performed [1,2], varying from 0.5 at 135K to a value close to 2 for $T > 350\text{K}$.

Statistical approaches [3,4] lead to exchange/hop ratios of 0.5. The statistical model was further generalized including a dynamical bias using quasi-classical trajectories using an approximation to overcome the zero-point energy leakage [5], leading to yields to hop/exchange ratio similar to the experimental ones [5].

Preliminary results will be presented using the Ring Polymer Molecular dynamics (RPMD) method[6] to include quantum effects.

1. M. Cordonnier, et al., J. Chem. Phys., 113, 3181, (2000).
2. N. Crabtree, et al, J. Chem. Phys, 134,194311, (2011).
3. K. Park and J. C. Light, J. Chem. Phys., 126, 044305, (2007).
4. E. Hugo and O. Asvany and S. Schlemmer, J. Chem. Phys., 130, 164302, (2009).
5. S. Gómez-Carrasco, et al., J. Chem. Phys., 137, 094303, (2012).
6. Y. V. Suleimanov, R. Colleparado-Guevara, D.E. Manolopoulos, J. Chem. Phys., 134, 044131, (2011).

*Speaker

Notes

The ortho:para ratio of the trihydrogen cation in diffuse molecular clouds

Kyle Crabtree * ¹

¹ University of California, Davis (UCD) – United States

Since its initial detection in the diffuse interstellar medium by infrared spectroscopy, the trihydrogen cation H_3^+ has been used as a probe of the physical conditions in its environment, such as the temperature and cosmic ray ionization rate. Its appeal as a physical probe derives from its apparently simple chemistry: in diffuse molecular clouds, it is formed following cosmic ray ionization of molecular hydrogen, undergoes spin-changing collisions with molecular hydrogen, and is destroyed primarily by dissociative recombination with electrons. Yet the spin temperature of H_3^+ (20-30 K) differs substantially from that of H_2 (50-70 K) in diffuse molecular sightlines in which both species have been observed, indicating an excess of para- H_3^+ that so far has not been satisfactorily accounted for in chemical models. In this talk, I will review the nuclear spin effects in the chemistry of H_3^+ as revealed by experiments, and discuss efforts to reproduce the astronomically observed excess of para- H_3^+ using both steady-state and time-dependent chemical modeling.

*Speaker

Notes

What do we know about time scales for the nuclear spin conversion in molecular ices and at the solid-gas interface?

Xavier Michaut * ¹, Thomas Putaud ¹, Audrey Moudens ¹, Laurent Philippe ¹, Pascal Jeseck ¹, Mathieu Bertin ¹, Jean-Hugues Fillion ¹, Patrice Cacciani ², Jean Cosleou ², Peter Cermak ³, Cedric Pardanaud ⁴

¹ Laboratoire d'Etudes du Rayonnement et de la Matière en Astrophysique et Atmosphères (LERMA) – CNRS : UMR8112, Université Pierre et Marie Curie (UPMC) - Paris VI, Université de Cergy Pontoise, Observatoire de Paris, Sorbonne Universités, PSL – 61, avenue de l'Observatoire - 75014 PARIS, France

² Physique des Lasers, Atomes et Molécules (PhLAM) – CNRS : UMR8523, Université Lille I - Sciences et technologies – Bat. P5 - Université de Lille1 - 59655 Villeneuve d'Ascq - France, France

³ Comenius University, Math Phys & Informat, Dept Expt Phys – Bratislava 84248, Slovakia

⁴ Physique des interactions ioniques et moléculaires (PIIM) – Aix Marseille Université, CNRS : UMR7345 – Case 232 Av escadrille Normandie-Niemen 13397 MARSEILLE CEDEX 20, France

H₂O and other hydrogenated molecules of astrophysical interest like H₂, CH₄, H₂CO, NH₃, CH₃OH, or C₂H₄ play an important role for the chemistry in the interstellar medium (ISM) and in protostellar nebulae. Because of the spin 1/2 of protons, these molecules exist in different nuclear spin configurations. The nuclear spin states are very stable in general. Thus, the exchange of one species to another – by flipping the spin of one or more of the equivalent atoms – is not very favored in the nature. In the tail of comets and in the interstellar medium (ISM), the *Ortho-to-Para Ratio* (*OPR*) does not always respect the value expected at thermodynamic equilibrium. It corresponds to a so-called “spin” temperature, different from the rotational temperature of the medium in which the molecules are observed. It seems then *OPR* is very dependent on the environment and history of the molecules (chemical formation, reactive collisions, adsorption / desorption cycles, nonreactive collisions). The characteristic time of the Nuclear Spin Conversion (*NSC*) of a molecular species to another through different states of matter becomes a critical factor.

During this talk, I will provide an update of the studies that were performed in the laboratory for the Nuclear Spin Conversion (*NSC*) of H₂, CH₄ and H₂O at low temperatures through non reactive processes. *NSC* requires an inhomogeneous magnetic field to flip the nuclear spin of a proton of the molecule and electrical interactions with the medium to transfer the excess of rotational energy. We show that in the case of low-temperature environments (called rare gas matrix), the *NSC* characteristic times vary from a few minutes to several hours in temperature range between 4 and 30 K. *NSC* is strongly dependent on the molecule and the physical conditions of its environment (temperature, concentration, crystal structure). We were able to identify the laws of temperature trends and to develop models that can account for the concentration behavior. A magnetic interaction potential between water molecules was constructed and confronted with the experimental data. Extrapolation to pure ice is in favour of a very rapid *NSC* in icy mantle.

*Speaker

When water (or methane) vapor interacts with its solid phase, the *OPR* changes slightly in the time scales accessible in the laboratory (from a few microseconds to a few seconds). The *OPR* in a biphasic medium at low temperature is balanced with the value determined for the isolated molecule even if saturation vapor pressure varies over 6 orders of magnitude. The solid phase seems to have small influence on the vapor. In the case of H₂ on ice surfaces at 10 K, the *NSC* takes place in several hours in the absence of paramagnetic doping. It is faster than in solid hydrogen and is probably catalyzed by the interaction with the surface.

These results open the way for studies in water ice which is an important subject considering the numerous observations of water made in the *ISM* and comets by Herschel telescope. These studies will find their extension in the development of new experiments: (1) to prepare ices enriched in one of nuclear spin species using optical pumping techniques and (2) to measure the survival of the *OPR* during ice desorption induced by *VUV* radiation.

Notes

Spin states of H_2D^+ and D_2H^+ as chemical age tracers

Olli Sipilä * ¹

¹ Max Planck Institute for Extraterrestrial Physics (MPE) – Germany

One of the long-standing problems in understanding the star formation process is knowing what the typical lifetimes of molecular clouds and cloud cores are. Different indicators of the (chemical) ages of molecular clouds or starless cores have been proposed, for example the $\text{N}_2\text{D}^+/\text{N}_2\text{H}^+$ abundance ratio. To obtain a reliable method of age estimation one needs an age tracer that is as independent of the physical conditions as possible. One such method pertains to the spin states of H_2D^+ because of the relatively simple relationship between the ortho/para ratios of H_2D^+ and H_2 . In this talk I will discuss recent efforts to derive a chemical age for the protostellar system IRAS 16293-2422 A/B using detailed models of spin-state chemistry. Here, observations of the spin states of both H_2D^+ and D_2H^+ in conjunction with chemical modeling allow us to constrain the chemical age. I will also summarize other recently completed and ongoing projects on the subject of (H_3^+ etc.) spin-state chemistry in starless cores.

*Speaker

Notes

Do spin temperatures differ between molecules in comets? The case for H₂O, CH₄, NH₃, C₂H₆ and CH₃OH

Geronimo Villanueva * ¹

¹ NASA Goddard Space Flight Center (NASA Goddard Space Flight Center) – Planetary Systems Laboratory NASA - Goddard Space Flight Center Code 693, B34:C189, Greenbelt, MD 20771, United States

It is perceived that all molecules in comets indicate a common spin temperature of ~30K. Is this value common to all molecules? How statistically significant and representative is this number to the general cometary population? Spin temperatures (T_{spin}) are measured by actually performing measurements of spin-isomeric ratios (R_{spin} , e.g. ortho/para). The relationship between T_{spin} and R_{spin} is asymptotic, and thus small linear errors in R_{spin} (or their underestimation) have substantial impact on the inferred T_{spin} . More importantly, molecules display different T_{spin} vs. R_{spin} relationships, and if T_{spin} is a cosmogonic indicator, all should indicate a common T_{spin} although derived from substantially different R_{spin} values.

To expand this test to many molecules, we present new methodologies for extracting spin temperatures from ethane (C₂H₆), methane (CH₄), and methanol (CH₃OH), and advanced new models for ortho/para water (H₂O) and ammonia (NH₃). Our H₂O analysis is based on the most complete fluorescence radiative transfer model to date, which incorporates 1,200 million transitions including those originating from high-energy levels that are activated in comets via non-resonance cascade. In a similar fashion, we developed non-resonance fluorescence models for NH₃ and HCN, and quantum band models for the ν_7 band of C₂H₆ and ν_3 band of CH₃OH. All models respect spin symmetry non-conversion radiative rules, and make use of a realistic Solar spectrum for the computation of fluorescence pumps.

We applied these new methods to derive spin-isomeric ratios for H₂O, CH₄, C₂H₆, CH₃OH and NH₃ on several high-quality cometary datasets. We compare our results with the measured organic compositions for these comets, and present possible formation and evolution scenarios.

*Speaker

Notes

Spin-state chemistry of deuterated ammonia

Jorma Harju * ^{1,2}, Olli Sipilä ¹, Paola Caselli ¹

¹ Max-Planck-Institut für extraterrestrische Physik (MPE) – Germany

² Department of Physics, University of Helsinki – Finland

Ammonia and its deuterated isotopologues are among the very few tracers of the physical and chemical conditions inside pre-stellar cores where stars and planets form. To fully exploit observations of these species, one should understand their formation. The spin ratios of molecules with identical nuclei can provide information of their origin; for example, grain-surface and gas-phase reactions are predicted to result in significantly different ortho/para ratios of NH₂D. We have developed a gas-grain chemistry model which distinguishes between different spin species of light hydrogen molecules, ammonia, water, and their deuterated variants. The model has been and is being tested through NH₃, NH₂D, NHD₂, and ND₃ observations towards pre-stellar cores. While successful in many respects, our model cannot reproduce the observed spin ratios of NH₂D and NHD₂ in the observed targets. Either the gas-phase reaction scheme needs to be revised or the contribution of grain-surface reactions to the formation of deuterated ammonia is under-estimated.

*Speaker

Notes

Nuclear Spin Isomers in Cometary Molecules: Survey for Ortho-to-Para Ratios of Ammonia in Comets

Hideyo Kawakita * ¹, Yoshiharu Shinnaka ²

¹ Koyama Astronomical Observatory – Kyoto Sangyo University, Motoyama, Kamigamo, Kita-ku, Kyoto 603-8555, Japan

² National Astronomical Observatory of Japan (NAOJ) – 2-21-1, Osawa, Mitaka, Tokyo 181-8588, Japan

Nuclear spin isomers ratios in cometary molecules have been interested as a cosmogonic indicator for the origins of cometary molecules. We performed the survey for ortho-to-para ratios (OPRs) of ammonia in comets based on high-resolution spectra of NH_2 in comets for more than 15 years. Our results show that the cometary OPRs of ammonia is different from the high-temperature limit (1.0 for ammonia) and ~ 1.15 , interpreted as a nuclear spin temperature of ~ 30 K. However, the $^{15}\text{N}/^{14}\text{N}$ ratios of ammonia estimated from the observations of NH_2 is enriched by a factor of ~ 3 compared with proto-solar values (this fact indicates much lower temperatures, $\lesssim 10$ K for the molecular formation of NH_3). The real meaning of the OPRs of ammonia in comets is discussed based on recent laboratory studies.

*Speaker

Notes

Spin Effects in Molecular Clouds

Steven Charnley * ¹

¹ NASA Goddard Space Flight Center (NASA Goddard Space Flight Center) – United States

I will discuss how chemical reactions involving different spin-states could produce observable effects in cold molecular clouds.

*Speaker

Notes

Ortho-to-para ratios as powerful interstellar diagnostics

Romane Le Gal ^{*} ¹, Eric Herbst ¹, Changjian Xie ², Hua Guo ², Dahbia Talbi ³, Carina Persson ⁴, Sebastien Muller ⁵

¹ Department of Chemistry, University of Virginia (UVA) – McCormick Road, Charlottesville, Virginia 22904, United States

² Department of Chemistry and Chemical Biology, University of New Mexico (UNM) – Albuquerque, New Mexico, 87131, USA, United States

³ Laboratoire Univers et Particules de Montpellier (LUPM) – CNRS : UMR5299, Université Montpellier II - Sciences et techniques, IN2P3 – Université de Montpellier II Place Eugène Bataillon - CC 72 34095 Montpellier Cédex 05, France

⁴ Chalmers University of Technology (Chalmers) – Chalmers University of Technology SE-412 96 Gothenburg Sweden, Sweden

⁵ Department of Earth and Space Sciences, Chalmers University of Technology, Onsala Space Observatory, SE-43992 Onsala, Sweden – Sweden

In the last decade, nuclear-spin astrochemistry has gained interest owing to numerous ortho-to-para ratio (OPR) measurements. These measurements have been made possible by the spectroscopic windows opened by the new era of telescopes with unprecedented sensitivities and high spectral resolution, giving access to previously elusive molecular lines. After the first OPR detection for H₂CO in dense molecular clouds [1], it took until the past decade, when OPRs of dual- and multi-hydrogenated species were observed, including H₃⁺, CH₂, C₃H₂, H₂O, NH₃, NH₂, H₂S, H₂CS, H₂O⁺ and H₂Cl⁺. OPRs are only functions of the temperature in thermal equilibrium and since spontaneous conversion between ortho and para states is extremely inefficient regarding the average lifetime of molecular clouds, OPRs were commonly believed to reflect a "formation temperature" [2, 3]. However, some of the newly observed OPRs listed above were found to be consistent with their thermal values while others, such as those of water [4, 5], H₃⁺ [6], NH₃ [7] and NH₂ [8], were not. In addition, an OPR of 3:1 for two-hydrogen molecules can refer to either a high-temperature limit or a statistical result. Hence, it becomes essential to determine how OPRs are produced to properly constrain the information that such new probes can provide. For this purpose, a comprehensive analysis of the processes governing the interstellar nuclear-spin chemistry of simple polyatomic species is needed, including the formation and possible conversions of the different spin symmetries both in the gas and solid phases. Once well understood, OPRs could afford new powerful astrophysical diagnostics on the chemical and physical conditions of their environments, and in particular could trace their thermal history, provided that the memory of a chemical process can be propagated and preserved in the molecular level population distributions.

It thus appears crucial to better understand the effects of nuclear-spin on chemical modeling in order to improve our understanding of the synthesis of non-equilibrium OPRs. In that sense, the recent observations of non-thermal values for the OPR of the radical NH₂ toward four high-mass star-forming regions [8], and a 3:1 value measured for the H₂Cl⁺ OPR toward diffuse and denser

*Speaker

gas [9,10], led us to develop detailed studies of the mechanisms involved in obtaining such OPRs with the aid of quasi-classical trajectory calculations [10,11]. We will present these new results, which should help to improve our comprehension of the interstellar medium.

1. Kahane et al. 1984, A& A, 137, 211
2. Mumma et al. 1987, A&A, 187, 419
3. Hama et al. 2016, Science, 351, 65
4. Lis et al. 2013, JPCA, 128 A, 117, 9661
5. Flagey et al. 2013, ApJ, 762, 11
6. Crabtree et al. 2011, ApJ, 729, 15
7. Persson et al. 2012, A&A, 543, A145
8. Persson et al. 2016, A&A, 586, A128
9. Neufeld et al. 2016, ApJ, 807, 54
10. Le Gal et al., in prep
11. Le Gal et al. 2016, A&A, 596, A35

Notes

The ortho-to-para ratios measured for triatomic hydrides in the diffuse interstellar medium

David Neufeld * ¹

¹ Johns Hopkins University (JHU) – United States

Recent observations of triatomic hydrides in the diffuse interstellar medium, including H_2O , H_2Cl^+ , and H_3^+ , provide valuable determinations of the ortho-to-para ratio (OPR). These observations will be reviewed, and the OPRs thereby derived will be discussed in the context of astrochemical models for diffuse clouds.

*Speaker

Notes

List of participants

- Ayotte Patrick
- Black John
- Bonev Boncho
- Bron Emeric
- Cermak Peter
- Charnley Steven
- Crabtree Kyle
- Faure Alexandre
- Fukutani Katsuyuki
- Georges Robert
- Gerlich Dieter
- González-Lezana Tomás
- Hama Tetsuya
- Harju Jorma
- Hily-Blant Pierre
- Kawakita Hideyo
- Le Gal Romane
- Legrand Martin
- Lis Darek
- Michaut Xavier
- Neufeld David
- Pineau Des Forets Guillaume
- Putaud Thomas
- Rist Claire
- Roncero Octavio

- Roueff Evelyne
- Schmiedt Hanno
- Sipilä Olli
- Villanueva Geronimo
- Wiesenfeld Laurent
- Wirström Eva

List of sponsors



Institut de Planétologie et d'Astrophysique de Grenoble (IPAG)



Observatoire des Sciences de l'Univers de Grenoble (OSUG)



Université Grenoble Alpes



Physique et Chimie du Milieu Interstellaire (PCMI)



**GRENOBLE - ALPES
MÉTROPOLITAIN**

Grenoble-Alpes Métropole