Report on the workshop "Nuclear Spin Effects in Astrochemistry" in Göteborg June 9-11, 2014.

Organization

The scientific programme of the workshop took place at Chalmers campus in Göteborg (lecture room EA) from lunch Monday June 9 to lunch Wednesday June 11, 2014, hosted by the Department of Earth and Space Sciences. On Wednesday afternoon participants were invited to join a visit to Onsala Space Observatory, hosted by the Swedish National Facility for Radio Astronomy.

There were 40 registered participants, of whom 18 were invited speakers - each giving a 30 minute presentation - and three (3) gave 20 minute contributed talks. Although not originally planned for, upon request two posters were given space to be presented during the breaks. It can also be noted that ten (10) of the registered participants belonged to the hosting department, while six (6) others were affiliated with other Swedish departments in Stockholm and Göteborg. The workshop was very interdisciplinary, with researchers from astrophysics, experimental atomic/molecular physics, theoretical chemistry, and planetary sciences.

A booklet containing the detailed workshop programme, talk abstracts, and list of participants was handed out to participants and is attached to this report for reference. See also the workshop webpage[1] where many of the talks are published as pdf links under the heading *Presentations*.

Scientific content

The scientific programme was divided by topic into five sessions, each consisting of a number of talks and followed by a general 20-30 minutes discussion.

After an introduction to the workshop and a review of the history of spin and its role in astrochemistry, the first session was devoted to experimental investigations of spin behaviour of H_2 and water in the interface between the solid and gas phase. We learned that low temperature (10 K) experiments show that the ortho-to-para conversion time for H_2 on water ice, as well as for water in an argon matrix, is rather short (few hundred minutes). However, the study of thermal desorption of pure water ice at these low temperatures is complicated. Water molecules deposited at 8 K onto amorphous solid water and desorbed at 150 K show an ortho-to-para ratio (OPR) =3, not equilibrated at the much lower formation temperature. For photodesorption, the different mechanisms by which water may be desorbed were reviewed, and it was concluded that only a fraction of all incoming photons affecting H_2O molecules will result in the desorption of an H_2O molecule - and out of these only a part can be expected to preserve the OPR aquired in the ice. The issue was raised whether water molecules in solid state even can be said to have an ortho/para spin state identity since they cannot rotate freely due to the hydrogen bonds.

The second session explored what investigations of ortho-para effects in the gas-phase are being conducted and what might be possible in the future, mainly using ion traps and ion storage rings. For example, results for the highly important OPR conversion reaction H^++H_2 were discussed as well as the spin-type dependence in H_3^+ and anion-H_2 complexes like Cl^--H_2. Possibilities to use the DESIREE facility in Stockholm to study astrophysically important mutual neutralization reactions, like CN^- with simple hydrocarbon ions which might be of importance in cometary comae, were discussed.

Theoretical studies of effects and methods based on varying OPR (of mainly H_2) in gas-phase interstellar environments were reviewed in the following session. In particular, at temperatures around 10 K the equilibrated H_2 OPR is less than 1%, which significantly affects the deuteration of molecules, as well as the nitrogen hydride formation and ^{15}N fractionation. Consequences of choosing

[1] http://www.chalmers.se/en/conference/Nuclear-spin-effects-in-Astrochemistry/Pages/default.aspx

different initial compositions and including/excluding time-dependence and/or dynamics in chemical models of these effects in star-forming clouds were discussed.

After lunch on Tuesday the focus moved from processes to astronomical observations and started with those on a more local scale - of comets. Traditionally, the measured OPR of water in comets (and to a lesser extent NH_3, CH_4, CH_3OH) has been used to derive the corresponding equilibrium temperature, the spin temperature. Most comets have reported spin temperatures clustered around 30 K, but we learned that by careful modelling of observed IR spectra, taking into account statistics and errors, this might not be at odds with a high temperature equilibrium OPR of 3. The only thing that can be said for certain is that no comets with very low (<20 K) spin temperatures have been found so far.

During the last session on galactic and extragalactic observations of nuclear spin ratios the impact on this field of absorption studies with Herschel Space Observatory was evident. While galactic OPRs in e.g. H_2O, H_2O^+, NH_3, H_2Cl^+ are most conveniently studied in diffuse gas toward strong continnum sources in the galactic plane with HIFI, extragalactic ratios towards ultra luminous infra-red galaxies can be determined from sets of absorption lines with PACS. For water, a range of OPR values are reported, of which most are consistent with the high-temperature equilibrium value of 3, given the uncertainties. With a few exceptions, high temperature equilibrium spin ratios are also found for other molecules. An exception that remains after careful analysis of systematic errors is gas at negative velocities towards the galactic center where the water OPR is 2.34 ± 0.35 (2σ errorbars). Another result that stands out are ammonia OPR's of 0.5-0.7 observed toward at least two galactic sources (G10.6-0.4 and W49N). While the high-temperature equilibrium OPR in ammonia is equal to unity, this value is expected to increase below $\sim$60 K (at thermal equilibrium). In a para-enriched H_2 gas, however, nuclear-spin selection rules have been shown to drive the OPR of ammonia below unity.

Scientific outcome

Most importantly, no very low water OPR values have yet been observed in the ISM and the same is the case for cometary water! Possibly this is because the desorption mechanism does not preserve the OPR - a notion which is also supported by experiments - which would mean that the formation temperature of comets cannot be probed by the spin temperature. This would also mean that the use of gas-phase OPRs to discern between gas-phase and grain surface formation of molecules currently lack theoretical support.

Exceptional care has to be taken in inferring OPRs or spin temperatures from observational data – published errorbars can be misleading unless clearly defined, and the datapoints consistent with high temperature equilibrium have to be included in any statistics.

It was concluded that in order to really understand spin behavior at solid-gas transitions, methods for separating between different desorption mechanisms in the experiments would be needed, and this presents a true challenge to the lab community. For chemical models to reproduce observed patterns and be used to infer formation paths, these processes need to be included - as well as separate reaction rates for all major reactions involving o/p-H_2. Not enough data are currently available for this to be done.

It was repeated several times during the workshop that nuclear spin effects in astrochemistry have needed interdisciplinary discussion like this for a long time. After several speakers made clear that more important results were under way and were to be presented "at the next meeting", plans are already now being drawn for a follow-up meeting in two years' time in France. To conclude, we would like to cite a statement made by Prof. Takeshi Oka (Univ. of Chicago) in the first invited talk of the workshop: *"This may be a small meeting, but a very important, historic meeting."*