ISSI proposal - 2007

A new generation of databases for interstellar chemical modeling in preparation for HSO and ALMA

Abstract:

One major question of solar system history concerns the relation between the chemical complexity observed in the interstellar medium and the prebiotic molecules in comets and on Earth during the appearance of life. This question may find some answers during the next ten years because of two future observational instruments: the Herschel Space Observatory (HSO) and the Atacama Large Millimeter Array (ALMA). By giving access to a range of frequencies not accessible from the ground, HSO will certainly permit the detection of many new molecules. In addition to finding new molecules because of its high sensitivity, ALMA will improve our understanding of the conditions of molecular formation in protostars and protoplanetary disks thanks to very high spectral and spatial resolution. In order to understand these future high-quality data, we will need chemical models of much higher quality than those in use today.

To improve existing models so that we can begin to cope with the large amounts of high-quality data obtainable from HSO and ALMA, we need to improve interstellar chemical databases in a variety of ways, but most importantly in the definition of the precision of reaction rate coefficients and branching fractions between different pathways so that accurate uncertainties in the results of models can be determined. To bring about this desired result, we propose to create a group of about ten specialists in the complementary fields of experimental chemical kinetics, ab initio quantum chemical calculations, and the chemical modeling of interstellar clouds. This group will for the first time bring expert opinion to bear on the uncertainties of the rate coefficients contained in the currently existing databases.

Scientific justification:

Our Sun and the planets of our solar system were born more than 10^9 years ago from interstellar dust and gas. The evolutionary stages of this process are reasonably well understood, thanks in part to the use of molecules and their chemistry as probes of physical conditions. Stellar evolution starts with diffuse interstellar matter, composed of refractory grain cores and atoms, which condenses into denser and colder clouds. In these clouds, atoms react to form molecules and icy mantles of molecules cover the dust grains. When these clouds start to collapse, they eventually heat up and lead to the formation of a protostar. Around this newly-forming star, the ices evaporate, and a rich organic chemistry takes place. A variety of organic molecules containing species such as methanol, CH_3OH, ethanol, C_2H_5OH, dimethyl ether, CH_3OCH_3, acetic acid CH_3COOH, and ethyl cyanide, C_2H_5CN are observed in the first phases of this collapse (Cazaux *et al.* 2004). It was in this environment surrounding a newly-formed star that first a protoplanetary disk and then planets and comets of our solar system were formed. To explain the whole picture of planetary formation and the origin of life, we need to understand accurately the physical conditions of all of the evolutionary stages starting from diffuse interstellar matter. Elucidating these physical conditions requires in turn knowledge of chemical abundances since molecules are our best probe of quantities such as temperature and ionization

fraction. Although chemical abundances can be obtained by analysis of astronomical spectra, mainly in the radio and infrared, a deeper understanding of the evolution requires knowledge of the chemical processes that form and destroy molecules, since such a knowledge allows us to produce chemical models sensitive to not only present physical conditions but their history. The chemistry in these models derives from databases that contain a large list of chemical reactions of various types: ion-neutral and neutral-neutral processes, dissociations and ionizations by UV photons and cosmic-ray particles, dissociative recombination between molecular ions and electrons, etc. Nowadays, these models are able to compute the abundances as a function of time for about four hundred gas-phase species using more than four thousand reactions, many of which remain unmeasured in the laboratory.

Although significant progress has been made since such models were first created in the 1970's, our understanding of the relationship between the molecular complexity observed in the interstellar medium and the pre-biotic molecules in comets and on Earth during the appearance of life remains incomplete. Our partial understanding will be enhanced during the next ten years with two future observational instruments: the Herschel Space Observatory (HSO) and the Atacama Large Millimeter Array (ALMA), both of which are the product of international cooperation given their immense cost. HSO, to be placed in a solar orbit, will observe molecular emission in a frequency range (the so-called far infrared) not accessible from the ground whereas the millimeter interferometer ALMA, consisting of more than 50 radio telescopes, will enable us to probe molecules all over the universe with spectroscopic and spatial resolution never before achieved. The fact that we can observe larger wavelength bands with a better sensitivity will allow the detection of many new molecules, increasing our knowledge of the interstellar medium complexity. In addition, with its high spatial resolution, ALMA will reveal the chemical and physical structure, at very small scales, of the environment in which planets form. In such context, estimating the accuracy of the model predictions and increasing this accuracy is crucial, indeed a *sine qua non*, for scientists to maximize the utility of HSO and ALMA.

The concept of computing the theoretical uncertainties in molecular abundances is now well established in the study of planetary atmospheres (see for instance Dobrijevic *et al.* 1998, Carrasco *et al.* 2007), but such computations have been undertaken only recently for interstellar models (Vasyunin *et al.* 2004; Wakelam *et al.* 2005, 2006). Aside from the lack of knowledge in the structure of the model itself, uncertainties in the predictions of chemical models have several origins. One concerns the physical parameters: temperature, density and cosmic-ray and UV fluxes. Another source of uncertainties, intrinsic to models, is due to the rate coefficients of gas and surface reactions: every reaction rate contained in a chemical model is known with a limited accuracy. While the chemical evolution is computed, the reaction rate coefficient uncertainties are propagated and result in a predicted uncertainty characterized by a confidence interval on the computed abundances. Knowing such confidence intervals is a necessary condition to making a proper comparison with observations and thus obtaining useful information. This goal can be reached only if uncertainties on the parameters are specified in a consistent manner: overestimation of uncertainties can lead to unrealistic, or even physically unsound, predictions, whereas their underestimation is expected to produce a misleading precision. Unfortunately, the uncertainties reported for the rate coefficients in the standard databases of interstellar chemistry are often inaccurate, especially for reactions not studied in the laboratory, but sometimes even for studied reactions, if the experimentalists failed to provide their own estimates. . It has to be stressed out that the cost of the experiments prevents generally the experimentalists from making repeated measurements, and that the reported uncertainties result often from an educated guess. This opens the question of the

shape of the distribution (normal, lognormal, loguniform...) to be used in such cases. Some of the inaccuracies stem also from the implication of non-experts in database compilation.

Since the beginning of its creation in 1991, one of the two main interstellar chemistry databases, the so-called UMIST network (Millar et al. 1991), has contained estimates of the rate coefficient uncertainty for measured reactions. This accuracy is divided into five different categories: 1, uncertainty < 25%; 2, uncertainty < 50%; 3, uncertainty within a factor of 2; 4, uncertainty within an order of magnitude; 5, highly uncertain. In the 1999 version of the database (Le Teuff *et al.* 2000), accuracy for non-measured reactions was added. Very recently, this information was also added into the other main interstellar chemical database, known as osu.2005. In both networks, most of the reactions have an uncertainty factor of 2. Wakelam *et al.* (2006) compared the two databases, rate99 (the UMIST version of 1999) and osu.2003 (the osu version of 2003) in a study of the chemistry of cold and dense interstellar clouds. The authors showed that, at a temperature of 10 K, almost half of the reactions present in both databases have a difference in rate coefficient larger than the reported uncertainty. The differences in rate coefficients between the two databases are due to different estimates for poorly understood reactions, different choices of experimental values, or different approximations for the temperature dependence of reactions measured at higher temperatures. Although recent update of both networks decreased the number of discrepancies, the remaining differences are not covered by the uncertainties listed in the databases. Such differences confirm the point that the current uncertainties are not well-defined. In addition to the gas-phase reactions – listed in osu and UMIST – reactions at the surface of interstellar grains are now known to be highly important. For this reason, we will also address this difficult problem of uncertainties in grain-surface chemistry, which has never been discussed up to now.

Chemical databases contain thousands of reactions and all of them cannot and do not need to be considered. In order to select important gas-phase and grain surface reactions to focus on, we are currently applying sensitivity methods, as previously used in Wakelam et al. (2006). Once this is accomplished, it is imperative that experts look at and improve both the important rate coefficients chosen in the databases used by astrochemists as well as their uncertainties. To accomplish this worthy goal, we propose the creation of a group of specialists in the complementary fields of experimental chemical kinetics, ab initio quantum chemical theory, surface chemistry, statistics, and the chemical modeling of interstellar clouds.

References:

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List of confirmed participants

Neutral-neutral reactivity at low temperature:

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Ion-neutral reactions:
4 Prof. Dieter Gerlich (Technische Universitaet Chemnitz, Germany)

Dissociative recombination:
5 Wolf Dietrich Geppert (Stockholm University, Sweden)

Photoreactions:
6 Prof. Ewine van Dishoeck (Leiden Observatory, The Netherlands)

Surface chemistry:
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Theoretical calculations:
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Uncertainty analysis methodology:
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Chemical modeling and databases:
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12 Prof. Eric Herbst (The Ohio State University, USA)
13 Andrew Markwick-Kemper (University of Manchester, UK)
14 Valentine Wakelam (Laboratoire d'Astrophysique de Bordeaux, France)

In total, there are 14 participants from 8 countries

Expected output

The current major databases used as input in models of interstellar chemistry contain uncertainties in their rate coefficients that include many poor estimates and downright guesses. In order to calculate reliable uncertainties in molecular abundances, it is necessary to start with consistent uncertainties in rate coefficients. By bringing together experts from several communities, we expect to improve these uncertainties in rate coefficients to a significant degree. With such vastly improved uncertainties, the databases will be much more useful to scientists in the calculation of molecular abundances and their uncertainties for a variety of sources in interstellar clouds, in particular those on the evolutionary path from dense clouds to stars and planets. Thus, our work will have a continuing and large impact on the databases for interstellar chemistry. Improved results from models of the chemistry based on the databases will in turn result in a much better understanding of the physical conditions pertaining to sources of star and planetary formation. Initially, we expect to write a review paper about uncertainties in chemical modeling for the interstellar medium in the journal Space Science Reviews. On a longer time scale, a significant number of other publications both in the astrophysical and chemical literature are expected as an outgrowth of this effort.

Schedule of the project

We intend to convene two one-week workshops over a period of 12 months:

- The first one would be early January 2008. The general context of astrochemistry will be presented and each participant will describe the sources of uncertainties in his own experimental or theoretical field. At the end of this first workshop, or shortly thereafter, we would have available accurate uncertainties for all important reactions that have been studied in the laboratory, and better estimates for other important reactions that, although not yet studied, are analogous to the studied ones.

- The second meeting could take place on September or October 2008. In the interim between the two meetings, panel members would consider the more exotic types of reactions in the databases, and whether or not the uncertainties in their rates are reasonable.

Added value of ISSI to the Team activity

The problem of uncertainties in interstellar chemical modeling requires the combination of several fields such as experimental chemistry, statistics and astrophysics. Our team is composed of scientists from multiple disciplines all over Europe and across the Atlantic. ISSI will provide to the team the possibility to convene in order to exchange different point of views of the same problem.

Facilities required and financial support requested of ISSI

Wifi internet connection for the laptops, two local computers and an overhead projector would be required. We would need financial support for all members (14 participants) for the two meetings of 5 days each.