The First Working Group 4 Meeting of the COST Action MOLIM: Molecules in Motion

"Active Databases"

BOOK OF ABSTRACTS

July 25, 2015

Windsor – United Kingdom

CMST COST ACTION CM1405

MOLECULES IN MOTION (MOLIM)

Interpretation of sophisticated experiments often requires advanced theories. A consistent set of user-friendly tools for an elaborate treatment of nuclear motions of microscopic and macroscopic systems does not yet exist. Development of the armoury of first-principles nuclear motion theory, via the advancement of theories, algorithms, and codes, is the major goal of this Action, with special emphasis on quantum effects involving electrons as well as nuclei. Molecular scientists, modellers and engineers will all benefit from the new methods and codes. The developments cover quantum chemical, quantum dynamical, semi-classical, and advanced classical treatments. Access to most of the source codes developed within the Action is provided to the scientific community free of charge. Multifaceted collaborative efforts with experimentalists applying the pilot versions of the new tools is considered to be vital to the success of the Action. MOLIM is a platform for (a) development of an extensive, heavily interlinked collaboration network of theorists and experimentalists from more than 20 countries; (b) quick dissemination of important results to a large and growing scientific community; and (c) establishment of long-lasting EU-wide conferences and training schools, educating the next generation of users of the next generation of chemistry tools. Through its several activities MOLIM fully supports the Excellence and Inclusiveness policy of COST.

Program of the First WG4 Meeting

SATURDAY, July 25, 2015	
09:00 – 09:20	**Derek Homeier** *Molecular opacity in the atmospheres of cool stars, brown dwarfs and extrasolar planets*
09:20 – 09:40	**Holger Müller** *The Cologne Database for Molecular Spectroscopy, CDMS and the ExoMol Project*
09:40– 10:20	**Remco de Kok***Hot Jupiter atmospheres at high spectral resolution*
10:20 – 11:00	*Coffee break*
11:00 – 11:20	**Amanda Ross** *Laboratory spectroscopy of optical spectra of magnetically sensitive MH radicals*
11:20– 11:40	**Christian Hill** *Developing the ExoMol website for big data sets: large line lists, cross sections and* k*-coefficients*
11:40– 12:00	**Vincent Boudon** *Line-by-line spectroscopic modeling of small hydrocarbon molecules for planetary applications*
12:00– 12:40	**Iouli Gordon** *Equipping HITRAN and HITEMP for exoplanetary exploration*
13:00 – 14:00	*Lunch*
14:00 – 14:20	**Attila G. Császár** *MOLIM, MARVEL, RESPECTH, and beyond*
14:20– 14:40	**Sergei Yurchenko** *Progress report about WG4 activities*
14:40– 15:20	**Nigel Mason** *Virtual Atomic and Molecular Data Centre (VAMDC)*
15:20– 16:00	**Round-Table Discussion**

Derek Homeier
Universität Heidelberg
Germany

Molecular opacity in the atmospheres of cool stars, brown dwarfs and extrasolar planets

Molecular lines are the dominant opacity source for a wide range of conditions and spectral domains in the coolest stellar and all substellar photospheres, rivalled only in certain instances by collision-induced absorption and condensate opacity. Accurate modelling of the positions, strengths and shapes of the lines of numerous molecules with millions and sometimes billions of individual transitions is therefore a necessary ingredient for precise numerical simulations of the radiative transfer in these atmospheres, not merely for producing synthetic spectra, but for reproducing the entire spectral energy distribution and heating and cooling processes. For a number of major molecules, relevant due to their wide spectral coverage, such as H_2O, CH_4, NH_3, or their role in the heating of irradiated planetary atmospheres, such as TiO and VO, important advancements have been made in recent years or are still under way, thanks in large part to the work of the Exomol project. I will present examples of the impact of different molecular opacity sources and their present uncertainties on 1D atmosphere models and synthetic spectra. I shall also highlight their potential consequences for the heating and cooling behaviour in dynamical simulations like radiative hydrodynamics (RHD) or general circulation models (GCM). These properties can therefore also have an effect on observables like the global temperature distribution on irradiated planets or time variability in substellar objects.

I will conclude with an outlook on the role on non-equilibrium chemistry in determining molecular absorption in the coolest brown dwarfs and planets.

Holger Müller
Physikalisches Institut, Universitat zu Köln
Köln, Germany

The Cologne Database for Molecular Spectroscopy, CDMS

The catalog section of the CDMS contains line lists of molecules and atoms mostly related to radio astronomy. They refer mostly to rotational spectra, but also to rovibrational or fine structure data. Experimental data are scrutinized and modeled using established Hamiltonian models to create line lists as accurate as is possible. Founded more than 15 years ago, the CDMS contains data of almost 800 species, including data of minor isotopologs or in excited vibrational states. The CDMS is available online (www.cdms.de) and is participating in the Virtual Atomic and Molecular Data Centre (VAMDC, www.vamdc.org). The CDMS is an important contributor to other secondary (HITRAN, GEISA) or tertiary data resources (CASSIS, LAMDA, SPLATALOGUE). We will give an overview of the current status of the CDMS.

Remco de Kok
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The Netherland

Hot Jupiter atmospheres at high spectral resolution

Hot Jupiters orbit their host star at short orbital distances and, as a result, they have large orbital velocities. The radial velocity of the planet changes significantly over a time span of hours. Using high dispersion spectroscopy (R 100,000), this orbital motion of the planet can be used to disentangle the light from the planet and that from the star, for both transiting and non-transiting planets. At high spectral resolution, molecules in the atmospheres of exoplanets can also be uniquely identified, and possible additional motion, due to e.g. winds, can be studied. I will show our results from past and ongoing analyses of high dispersion spectra from VLT's CRIRES and UVES instruments. I will also discuss specific challenges in spectral modeling at high spectral resolution, and the requirements for molecular line lists.

Amanda Ross
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France

Laboratory spectroscopy of optical spectra of magnetically sensitive MH radicals

Some of the first-row transition metal monohydrides seen in sunspots and in the spectra of cool stars have been noted as possible probes of magnetic field, particularly for cool stellar objects. FeH, cited for example by Afram et al.[Astron. & Astrophys. 2008 482 387-95.], seems particularly promising in this respect, because of its strong Zeeman response in the near infrared. Laboratory spectra are required to supply reliable parameters for spectropolarimetric analysis of remote objects, but producing parameters appropriate for the equilibrium temperatures of 'cool' stellar objects - usually more than 3000 C and greatly in excess of temperatures accessible in the laboratory - is non-trivial. Forming such species at near-ambient temperatures has the advantage of reducing Doppler widths, and making it possible to resolve (at least partially) Zeeman structure within rotational lines. High-sensitivity spectroscopy is an asset in this context. Another major challenge is to model available data so that extrapolations to hotter conditions are plausible.

I will illustrate some of our recent work in this area, using spectra of FeH and NiH formed in a hollow-cathode sputtering source as examples. We have used cw laser excitation and Fourier-transform resolved fluorescence to study Zeeman patterns, working at magnetic fields between 0.3 and 0.9 Tesla provided by permanent magnets. Dispersed fluorescence spectra actually give access to the Zeeman response of lower-state levels that are not thermally accessible in the laboratory. This approach has the advantage of recording many transitions simultaneously, in identical conditions (magnetic field strength, pressure, laser polarisation...), but remains useful only for systems giving very strong emission.

Christian Hill
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Developing the ExoMol website for big data sets: large line lists, cross sections and k-coefficients

The ExoMol project [1] has, over the last four years, produced *ab initio*, high-temperature line lists for over 50 molecules, several of which exist in more than one isotopologue variants. These data are curated and provided to users through the ExoMol website, www.exomol.com.

Although the number of transitions for diatomic molecules is typically manageable by "traditional" methods such as simply listing them in a single text file, for larger molecules this approach is not practical. For example, the "10to10" line list for methane [2] contains almost 10 billion transitions. Such large data sets require novel approaches to their management, following techniques pioneered in the field of "big data".

This presentation will explore some of the software technologies available to assist with the management of large spectroscopic data sets. Under some circumstances, large line lists may be converted to absorption (or emission) cross sections at a specified temperature, pressure and resolution; indeed, the ExoMol website provides a service to generate these for users [3]. Related k-coefficient tables are popular with astronomers. Where this approach is not possible or suitable, alternative, more compressed data formats are available, starting with the "native" ExoMol format which separates states and transitions into distinct batches of files [4]. Beyond this, there exist binary formats such as HDF-5 and fully-fledged file-system based database frameworks such as Hadoop and Cassandra.

1. S. N. Yurchenko, J. Tennyson, "ExoMol: molecular line lists for exoplanet and other atmospheres", *Mon. Not. R. Astron. Soc.* **425**, 21 (2012).
2. S. N. Yurchenko, J. Tennyson, "ExoMol line lists IV: The rotation-vibration spectrum of methane up to 1500 K", *Mon. Not. R. Astron. Soc.* **440**, 1649 (2014).
3. C. Hill, S. N. Yurchenko, J. Tennyson, "Temperature-dependent molecular absorption cross sections for exoplanets and other atmospheres", *Icarus* **226**, 1673 (2013).
4. J. Tennyson, C. Hill, S. N. Yurchenko, "Data structures for ExoMol: Molecular line lists for exoplanet and other atmospheres", 8th ICAMDATA Conference, NIST, September 30 - October 4 (2012).

Vincent Boudon
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Line-by-line spectroscopic modeling of small hydrocarbon molecules for planetary application

Methane (CH_4) is a key constituent of many planetary atmospheres of the Solar System and has also been found in some "hot-jupiter" type exoplanets and in brown dwarfs. This molecule is therefore extensively studies from both experimental and theoretical point of views, using advances techniques. Theoretical variational calculations from the Reims and Exomol groups provide extensive line lists. However, a lot of work is still feasible and useful for line-by-line assignment and fit of experimental spectra, using effective Hamiltonian and dipole moments. This should be of great help to constrain the theoretical models. We present here the current status of such analyses for methane and its main isotopologues, including very recent results using high-temperature spectra. We also present similar studies performed on the ethylene (C_2H_4) molecule, in collaboration with the Reims group.

All our results are available through the VAMDC (Virtual Atomic and Molecular Data Centre) European portal (http://www.vamdc.org).

Iouli Gordon
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USA

Equipping HITRAN and HITEMP for exoplanetary exploration

The HITRAN spectroscopic database[1] is widely used in different fields of science and industry including exoplanetary research. Nevertheless, since most of the currently observable exoplanetary atmospheres are hot Jupiters, the HITEMP spectroscopic database[2] is more appropriate. The HITEMP database indeed has substantially more lines which enables modelling spectra at high temperatures. However, contrary to HITRAN which has 47 molecules in the line-by-line section, the HITEMP database has only five molecules, namely H_2O, CO_2, CO, NO and OH. However, one should note that the extent of HITRAN data for hydrogen halides and hydrogen itself does allow high-temperature modelling. It is important to update the existing molecular data in HITEMP, but also to add more molecules, in particular methane, ammonia, HCN, etc. At the meeting we will discuss what new additions one should expect from the next edition of HITEMP.

Finally, both HITRAN and HITEMP will soon be supplemented with the data on broadening and shifting of spectral lines due to the pressure of H_2, He and CO_2.

The HITRAN database is supported by the NASA Earth Observing System (EOS) under the grant NNX11AF91G, and by the NASA Planetary Atmospheres program under grant NNX13AI59G.

[1]L. S. Rothman, I. E. Gordon, et al. "The HITRAN 2012 molecular spectroscopic database," *JQSRT* **130**, 4-50 (2013).
[2]L. S. Rothman, I. E. Gordon, et al. "HITEMP, the high-temperature molecular spectroscopic database," *JQSRT* **111**, 2139-50 (2010).

Tibor Furtenbacher and Attila G. Császár

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MOLIM, MARVEL, RESPECTH and beyond

Following an exposure of the new COST action MOLIM (Molecules in Motion, CM1405, http://cost-molim.eu), recent algorithmic developments and subsequent results they made possible are described, focusing especially on the MARVEL (Measured Active Rotational-Vibrational Energy Levels) protocol developed in our group. The molecules to be covered include the water isotopologues $H_2{}^{16}O$, $H2{}^{18}O$, $H_2{}^{17}O$, $HD{}^{16}O$, $HD{}^{18}O$, $HD{}^{17}O$, $D_2{}^{16}O$, $D_2{}^{18}O$, $D_2{}^{17}O$, as well as $H_3{}^+$, H_2D^+, D_2H^+, $^{14}NH_3$, $^{12}C_2$, and parent ketene, H_2CCO, molecules for which MARVEL energy levels are available following a careful analysis and validation of all the related published high-resolution spectra. The efficient use of spectroscopic networks during the analysis and the predictive power of MARVEL are emphasized. At the end of the talk ReSpecTh, a new joint reaction kinetics, spectroscopy, and thermochemistry information system (http://respecth.hu) is described.