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Rotational Spectroscopy of Molecules of Astrophysical Interest

Studying the chemical inventory of star-forming regions provides unique information on the evolution of gas and dust during the formation of stars and planets [1]. Additionally, molecular emission and absorption can be used to measure fundamental physical properties such as temperature, density, and kinematics. Given that molecules are not homogeneously distributed across star forming regions, multi-molecular and multi-line observations allow to reconstruct both their 3D chemical and physical structures. The study of interstellar molecules flourished in the 1980s, and it developed in parallel with the millimeter receiver technology and to date, almost 300 different interstellar molecular species have been detected, ranging from simple diatomic to complex organic molecules. Excluding a few exceptions, all of these molecules have been detected through their rotational spectrum in the cm-, mm- and sub-mm-wave range. To interpret the steadily increasing amount of high-resolution astronomical data, high-resolution laboratory spectroscopy data are necessary. It is thanks to accurate spectroscopic data that in the last 60 years just few misidentifications happened. To firmly detect a new molecular species in space, prior (or subsequent) laboratory identification is mandatory. Furthermore, precise rest frequencies allow the spatial correlation of different species, which is very important for the consistency of astrochemical models.

Rotational spectroscopy is an important tool used to study the structure of molecules in the gas phase. Compared to vibrational and electronic spectra, rotational spectra are very selective because spectral superimpositions are very unlikely to occur. Given the high selectivity of rotational spectroscopy, it is often not required to have a purified gaseous sample. This is of particular importance in the case of unstable molecules such as ions that must be produced in situ in order for the spectrum to be recorded. High-accurate spectroscopic data are used to derive molecular parameters. Once the molecular parameters are derived, it is possible to predict the spectrum of a certain molecular species. The rotational spectrum has the unique advantage of being the fingerprint of the molecule and hence allows to make an unambiguous detection.

With respect to Earth, the ISM (interstellar medium) is characterised by very low pressure. High density in the ISM means 10^7

molecules cm^{-3} , while on Earth we have 10^{19} molecules cm^{-3} at sea level, and high vacuum is usually in the order of 10^{10} molecules cm^{-3} . Given the extreme conditions, and in particular the very low pressure, reactive molecules such as ions and radicals are widely present in the ISM, and they are of pivotal importance for the development of molecular complexity in space. Their importance was recognized already in the 70s, as soon as the first polyatomic molecular species were detected in the ISM [2]. The development of molecular complexity starts indeed from an ion, H_3^+ , that forms the basis for an extensive network of ion-molecule reactions that are responsible for the creation of most of the molecules observed in interstellar space. Ion-neutral reactions are mostly barrierless, and hence proceed very fast also in cold regions of the ISM. The first detection of H_3^+ confirmed this scheme for the interstellar chemistry [3].

Despite a large number of molecular species has been detected in the ISM, a lot of work still needs to be done, and a large number of molecular species still needs to be observed in the laboratory in order to be observed in space. In order to understand the increasing complexity of interstellar chemistry, chemical models that include tens of thousands of reactions and reaction rates are used. These models need to be constrained from both laboratory work and observations. To discriminate among different reactions schemes in the production of a particular molecular species, the observations of the molecule itself as well as of the reaction intermediates are crucial to test the chemical models and finally have a global picture of how molecular complexity builds up in space.

How far can molecular complexity go in star-forming regions, and how much of that complexity can be inherited by forming planets? These are fundamental questions in modern astrophysics, and they can only be addressed with a multidisciplinary approach that has laboratory spectroscopy at its core.

Complex organic molecules (COMs), defined as molecules with more than five atoms, containing carbon, oxygen and hydrogen, are ubiquitous in star-forming regions and have been observed around young stars as well as towards starless and pre-stellar cores (e.g. Ref. [4]), suggesting that molecular complexity undergoes a significant development prior to the ignition of the star.

In the past years, my research focused on the spectroscopy of deuterated isotopologues of key COMs, and I use the resulting spectral catalogs to detect these molecules in the ISM for the first time (e.g. CHD_2CHO , [5]). The long term goal of this project is to unveil the level of molecular complexity reached in the

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early phases of star formation, as well as the chemical reactions that drive the build-up of molecular complexity (included in chemical models).

Isotopic fractionation is the distribution of stable, less abundant isotopes in molecular species. Isotopic fractionation processes are very sensitive to variations of physical and chemical conditions and are therefore very precise tools for following the evolution of molecular material within the star and planet formation process. Deuterium fractionation, in particular, has proven to be an excellent tool for understanding the evolution of material from interstellar clouds to planets. An enhancement of the deuterium fractionation in molecules is a consequence of the cold temperatures in the center of a soon-to-collapse core (right before the formation of the protostar). Not just prestellar cores, but also protostellar cores show an enhancement in deuterated molecules either because they are inherited from the prestellar phase or because they are originally formed or deposited onto dust grain surfaces during the prestellar phase and then desorbed when the protostar switches on. Apart from being excellent tracers of the early stages of star formation, deuterated molecules can be used to determine the (chemical) age of a core because of the chemical changes that occur in the contraction of the cloud (i.e. the ortho-to-para H_2 ratio, which regulates the deuteration fraction).

To observe deuterated isotopologues of COMs in space and understand the chemistry that regulates their formation, as well as their origin within the star and planet formation process, laboratory spectroscopy is necessary. To study the rotational spectrum of deuterated COMs we used two spectrometers in the CAS laboratories at MPE: a chirped-pulse Fourier transform spectrometer and a frequency modulation absorption spectrometer. Both spectrometers have been used to study the spectroscopy of the doubly deuterated acetaldehyde (CHD_2CHO) and singly and doubly deuterated methyl mercaptan (CH_2DSH and CHD_2SH). Figure 1 shows a part of the spectrum of CH_2DSH recorded in the CAS laboratories with the FM absorption spectrometer in the upper panel and our model based on the experimental parameters and the well-known Hamiltonian for an asymmetric rotor in the lower panel.

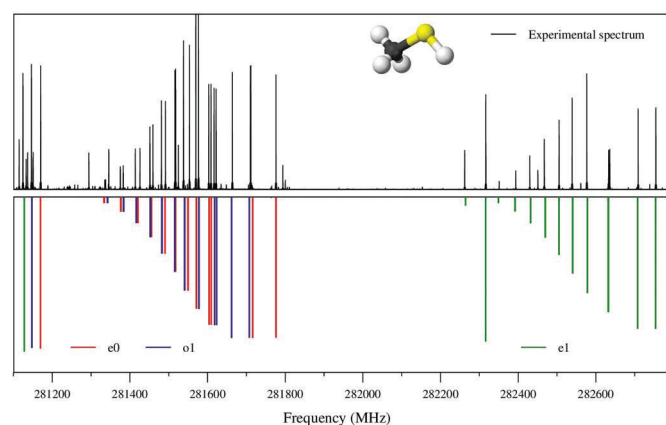


Fig. 1: Experimental spectrum (upper panel) and model (lower panel) of CH_2DSH . e_0 , e_1 , and o_1 are the three non-degenerate torsional levels of the vibrational ground state of singly deuterated methyl mercaptan.

Spectrometers Description

Chirped-pulse Fourier transform (CP-FT) microwave spectroscopy provides broadband spectral coverage on each single spectrum acquisition. The CAS laboratories operate a broadband Chirped-Pulse Fourier Transform Spectrometer (CP-FTS) covering the frequency regions 6–8 GHz, 18–26 GHz, 80–110 GHz, and 160–220 GHz. In CP-FT spectrometers, a gaseous molecular sample is polarised by a chirped pulse (of $\sim 1 \mu s$ duration) and the subsequent free induction decay (FID) of the molecular signal in the time domain is recorded with an instantaneous spectral bandwidth of several GHz. The spectrum is obtained by Fourier transformation of the FID. The capability to record broad scans with high frequency resolution and high dynamic range on microsecond timescales makes this instrument very suitable for studying the spectra of astrophysically relevant molecules, in particular if they have dense spectra (e.g. complex organic molecules, COMs) or if frequency predictions are very uncertain. The electronics are located in a movable rack, so that it can be most easily coupled to a variety of chambers/cells in the CAS laboratories at MPE, depending on the desired sample to study. The chirped pulse is generated by a 5 GHz arbitrary waveform generator (Keysight, M8190A). The signal is upconverted by an IQ modulator and subsequently amplified by a solid-state amplifier and fed into the sample chamber (e.g. glass cell). Subsequently, the molecular signal (FID) is first amplified (low noise amplifier) and downconverted in frequency (IQ mixer), before it is recorded either with a 25 GHz digital oscilloscope or 2.5 GHz digitizer card (Acqiris U5310A). A signal generator (Keysight E8257D) acts as local oscillator. Its signal is split by a power divider and fed into IQ modulator and the IQ mixer in the detection unit. The frequency extensions to 75–110 GHz and 160–220 GHz consist of active multipliers. A medium power amplifier allows to generate chirped pulses of about 250 mW and a low noise amplifier attached to the harmonic mixer is applied for downconversion.

The frequency modulation (FM) sub-millimetre absorption spectrometer is equipped with a 1.5 m long stainless-steel cell, as well as a 1.5 m long glass cell. The radiation source is an active multiplier chain (Virginia Diodes) that is driven by a synthesizer (Keysight E8257D) operating at centimetre wavelengths. Using a series of frequency multiplication stages, this set-up provides continuous coverage across the 82–1100 GHz frequency range. Accurate frequency and phase stabilisation are achieved by providing the synthesizer with a 10 MHz rubidium frequency standard (Stanford Research Systems). A liquid-He cooled InSb hot electron bolometer (QMC Instr. Ltd.) is used as a detector. Frequency modulation is achieved by modulating the carrier signal with a sine wave at a rate of 15 kHz, and then demodulating the detector output at $2f$ using a digital lock-in amplifier (SRS SR830). In this way, the second derivative of the actual absorption profile is recorded by the computer-controlled acquisition system.

Studying the budget of material available for the formation of planets in a wide variety of star-forming regions is of particular interest also given the recent developments in the observations of extrasolar planets. In the upcoming decades, the astrochemical community will be able to compare the rich chemistry observed in star-forming regions with chemical studies of exoplanetary atmospheres, thus moving towards a comprehensive and general picture of the process of forming Earth-like planets. Such developments will only be possible with a concerted effort of observational, theoretical and laboratory work.

References

- [1] Paola Caselli and Cecilia Ceccarelli: Our Astrochemical Heritage, *The Astronomy and Astrophysics Review* 2012 **20**, 56.
- [2] Eric Herbst and William Klemperer: The Formation and Depletion of Molecules in Dense Interstellar Clouds, *The Astrophysical Journal* 1973 **185**, 505-534.
- [3] Thomas R. Geballe and Takeshi Oka: Detection of H_3^+ in interstellar space, *Nature* 1996 **384**, 334-335.
- [4] Izaskun Jiménez Serra, Anton I. Vasyunin, Paola Caselli, Nuria Marcelino, Nicolas Billot, Serena Viti, Leonardo Testi, Charlotte Vastel, Bertrand Lefloch, Rafael Bachiller, The Spatial Distribution of Complex Organic Molecules in the L1544 Pre-stellar Core, *The Astrophysical Journal Letters* 2016 **830**, L6.
- [5] Judit Ferrer Asensio, Silvia Spezzano, Laurent Coudert, Valerio Lattanzi, Christian P. Endres, Jes K. Jørgensen, Paola Caselli, Millimetre and sub-millimetre spectroscopy of doubly deuterated acetaldehyde (CHD_2CHO) and first detection towards IRAS 16293-2422, *Astronomy & Astrophysics* 2023 **670**, A177.

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ZITATE ZUM UNIVERSUM

„Das Universum ist voller Magie, die nur darauf wartet, von aufmerksamen Augen entdeckt zu werden.“

Douglas Adams

„Blicke in den Himmelsraum und du wirst erkennen, dass das Universum unendlich ist, genau wie die Möglichkeiten, die es uns bietet.“

Stephen Hawking

„Der Schlüssel zum Verständnis des Universums liegt in unserer Neugier und unserem unermüdlichen Streben nach Wissen.“

Konrad Lorenz

„Das Universum ist nicht nur freundlicherweise so eingerichtet worden, dass wir darin existieren können, sondern auch freundlicherweise so eingerichtet worden, dass wir es verstehen können.“

Stephen Hawking

„Der Sinn des Universums liegt nicht darin, von uns ergründet zu werden, sondern darin, dass es uns ermöglicht, nach dem Sinn zu suchen.“

Albert Einstein

Quelle: <https://worldday.de/universum-zitate/>

„Wir dürfen das Weltall nicht einengen, um es den Grenzen unseres Vorstellungsvermögens anzupassen, wie der Mensch es bisher zu tun pflegte. Wir müssen vielmehr unser Wissen ausdehnen, so dass es das Bild des Weltalls zu fassen vermag.“

Francis Bacon

„Das Weltall ist ein Kreis, dessen Mittelpunkt überall, dessen Umfang nirgends ist.“

Blaise Pascal

„Das Universum ist vollkommen. Es kann nicht verbessert werden. Wer es verändern will, verdirbt es. Wer es besitzen will, verliert es.“

Laotse

„Wir müssen den gegenwärtigen Zustand des Weltalls als Folge eines vorangegangenen und Ursache seines nachfolgenden Zustands betrachten.“

Pierre-Simon Laplace

Quelle: <https://www.aphorismen.de/thema/Universum?seite=1>