# The Universe

## What is there? How much is there?

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e humans are curious and want to explore the universe in which we live as much as possible. We are located on Earth and have been able to visit the Moon so far, although an expedition to Mars is currently being seriously discussed. The flight time to Mars is at best several months and more distant parts of the universe are not accessible for human visits. These must therefore be investigated by remote sensing, i.e. by spectroscopy.

The universe consists of atoms and molecules. The molecules we are dealing with are located in the outer layers of stars, in interstellar space (i.e. the space between stars) and in exoplanets (which orbit stars other than the Sun and are currently being studied in detail). Remote sensing is used to determine what (i.e. which molecules) are present in the distant environment and how many (or how much) of these molecules there are. Electromagnetic radiation (light) from the distant environment is detected and analysed. Large investments are being made in equipment for such experiments, for example in the Atacama Large Millimeter/Submillimeter Array (ALMA) in the Atacama Desert of northern Chile. ALMA consists of 66 radio telescopes that were built between 2004 and 2014 for around 1.4 billion US dollars in cooperation between the European Southern Observatory (ESO) and organisations in the USA, Canada, Japan, South Korea, Taiwan and Chile.

Observatories like ALMA receive radiation from the remote regions of the universe that we want to study. By analyzing the radiation we aim at answering the questions about what and how much. The radia-

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Investigates the universe from afar: Prof. Per Jensen.

tion is recorded as intensity depending on frequency or wavelength and thus represents a spectrum. The structure of the spectrum is characteristic of the molecules that cause it. That is, as is often said, the structure of the spectrum provides the fingerprint(s) of the molecule(s) involved, and the intensity of the signal provides information about the amount of these molecules. The recording of a remote sensing spectrum can be compared to the investigation of a crime scene by the modern police. One finds fingerprints (and nowadays DNA samples) of the offender, just as the remote sensing spectrum provides the fingerprints of the "guilty" molecules. However, fingerprint/DNA samples from a crime scene only serve to find the culprit if a catalogue of fingerprint/DNA samples from possible perpetrators is available. Likewise, the interpretation of

remote sensing spectra requires a catalogue of fingerprints of molecules that may be present in the remote object under investigation. To answer the question of how much, we also need to know how much energy a single molecule absorbs or emits in a unit of time. If we then know the amount of energy absorbed or emitted by the molecules in the distant object per unit of time, we can calculate by a rule of three how many molecules are in our line of sight.

In principle, catalogues of molecular spectra can be determined in the laboratory. To do this, we have to prepare a gas phase sample of the given molecule and measure its spectrum with a laboratory spectrometer. To additionally determine the amount of energy absorbed or emitted per time unit and molecule, we have to prepare the sample with a known

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Fig. 1.: Part of the Atacama Large Millimeter/submillimeter Array (ALMA) at night.

concentration. Laboratory spectroscopy can be performed in the way described here for stable, long-lived molecules whose concentration remains unchanged over a longer period of time.

In practice, a large part of the astrophysically and chemically interesting molecules is unstable and shortlived. They must be produced in laboratory spectroscopy experiments during the experiment, e.g. by fragmentation of stable molecules by electrical discharges or irradiation with laser light. However, in such experiments we do not know whether we can produce the desired unstable molecule, and even if we can, we do not know the concentration of the unstable molecules formed. Therefore, we have to ask what and how much questions in connection with the laboratory spectroscopy experiment. This is where theoretical spectroscopy can help: we theoretically calculate the fingerprint of a molecule and the energy/time absorbed/emitted by a single molecule. Of course, we know for which molecule we do the calculations, and so our results can be used to answer the "what" and "how much" questions, both for laboratory and remote sensing spectra. The results of calculations of this type are compiled in socalled line lists, i.e. catalogues of calculated transition wave numbers and probabilities.

In order to answer the 'what' and 'how much' questions, we have to simulate the required molecule spectra theoretically. Molecules consist of nuclei and electrons, and the quantum mechanical simulations are carried out within the framework of the twostage, so-called Born-Oppenheimer approximation: First, electron structure or ab initio calculations are performed: The nuclei are fixed in space and the quantum mechanical problem of the electrons moving in the electrostatic (Coulomb) field from the nuclei and the other electrons is solved for many different arrangements of the nuclei in space. In Wuppertal we do not carry out method development in the area of ab initio theory, but use commercially available computer programs, especially MOLPRO, to obtain the Born-Oppenheimer potential energy function V, which depends on the nuclear coordinates only.

In the second step of the spectral simulations we solve the quantum mechanical problem of the nuclei moving in the Born-Oppenheim potential function. These calculations are carried out with programs developed or co-developed in Wuppertal, mainly with the program TROVE (Theoretical ROtation-Vibration Energies) whose development started around year 2000 in Wuppertal. Since then TROVE has been continuously developed with Dr. Sergei N. Yurchenko (19992001 postdoc in my group in Wuppertal, now Professor at University College London (UCL), UK) as the driving force. TROVE solves the time-independent Schrödinger equation

$$\hat{H} \psi_m = E_m \psi_n$$

for the nuclei. Only the Hamiltonian  $\hat{H}$  is initially known, it contains the potential function *V*. We are therefore looking for solutions  $(E_m, \psi_m)$  consisting of an allowed energy  $E_m$  and the corresponding wave function  $\psi_m$ , which depends on the nuclear coordinates. The index *m* numbers the solutions. The wave function is expressed as a superposition of known basis functions  $\varphi_k$  with initially unknown expansion coefficients  $c_{mk}$ :

$$\psi_m = \sum_{k=0}^{\infty} c_{mk} \varphi_k \approx \sum_{k=0}^{N} c_{mk} \varphi_k$$

With an infinite number of summands, this relationship would be exact. In practice, however, the expansion is truncated to obtain an approximate wave function with a finite number of summands N. The time-independent Schrödinger equation is thus expressed in matrix form as

$$\mathbf{H} \mathbf{c}_m = E_m \mathbf{c}_n$$

Here, **H** is a square matrix of the dimension *N*; its elements are known and depend on the functions  $\varphi_k$  and  $\hat{H}$ . The column vector  $\mathbf{c}_m$  contains the *N* initially

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Fig. 2.: Simulated absorption spectra of the methylene radical  $\rm CH_{3}$  and a view of the radical in its planar equilateral triangular equilibrium structure.

unknown expansion coefficients  $c_{mk}$ . The matrix equation can be solved by standard methods (often called diagonalization of matrix **H**) of linear algebra; we use commercially available computer routines optimized for our computers to obtain the allowed molecular energies  $E_m$  and the corresponding eigenvector coefficients  $c_{mk}$ .

When setting up the matrix **H**, we have a certain freedom in choosing the basis functions  $\varphi_k$ . It is convenient to choose these functions so that they reflect the existing *symmetries* of the molecule. In this case, **H** becomes block diagonal. It splits into smaller submatrices and each of these can be diagonalized separately, thus saving enormous amounts of computer time and storage space. A symmetry that exists for all molecules is *rotational symmetry*. An isolated molecule can be rotated freely in space without changing its energy (or, equivalently, its Hamiltonian). In TROVE we select basis functions that belong to the so-called irreducible representations  $\mathbf{D}^{(J)}$  of the infinitely large rotational symmetry group SO(3).  $\mathbf{D}^{(J)}$  is characterized by the quantum number J = 0, 1, 2, 3, ..., which defines the length of the angular momentum vector. We finally achieve that **H** splits into smaller blocks, each with a defined J value, and we can perform the calculation practically in a loop over *J*; the calculations for different *J* blocks are independent of each other.

In addition to rotational symmetry, we use in TROVE the fact that the Hamiltonian of the molecule remains unchanged when identical nuclei are permuted and when all particles of the molecule are inverted in the center of mass. This permutation-inversion symmetry produces the molecular symmetry group (MS group). TROVE uses the symmetry of the MS group to achieve a further block diagonal structure of the J blocks in the Hamiltonian matrix.



Fig. 2 shows the methylene radical  $CH_3$  and some simulated  $CH_3$  spectra at different temperatures. Line lists of  $CH_3$  have been recently calculated with TROVE as part of the doctoral thesis of Dr. Ahmad Adam, in collaboration with the research group of Prof. Sergei N. Yurchenko at UCL. At equilibrium  $CH_3$  is planar and the three protons form an equilateral triangle. The vibrations are relatively small displacements from the equilibrium structure.

Fig. 3 shows a general view of an ethane molecule  $H_3CCH_3$ . The six protons are numbered as 1, 2, .... 6. In another view of the molecule from one end, along the CC axis, we have marked the angle  $\tau$  defined as the dihedral angle between two planes, each of them containing both C nuclei and the proton 1 and 4, respectively. We also show the  $\tau$ -dependence of V. Ethane has three equivalent staggered equilibrium structures with  $\tau$ -values of 60°, 240° and 300°, respectively. The energy barriers between the three structures are relatively small and the molecule can, for example at room temperature, penetrate these barriers relatively effortlessly and move over the entire  $\tau$ -interval from 0° to 360°. In contrast to the vibration of CH<sub>3</sub>, the vibrational motion of H<sub>3</sub>CCH<sub>3</sub> cannot be described as small displacements from a single equilibrium structure: With H<sub>3</sub>CCH<sub>3</sub>, the  $\tau$ -motion is a large amplitude vibration, making the description of the rotation-vibration motion much more complicated. However, TROVE is currently able to treat molecules with one *large amplitude vibration* and we are currently preparing the calculations of ethane line lists by implementing the MS group symmetry of ethane in TROVE, again in collaboration with the Yurchenko group at UCL.

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