

ASTROLABORATORY IN ALCOI: USES AND POSSIBILITIES

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Abstract: Since 2001 an astrolaboratory for physical and chemical research has been building up in Alcoi (Spain). There are many ways to study materials present in space: astronomical observation, theoretical modelling and computational simulation; one important role of the laboratory is to complement them. It would hardly be an exaggeration to say that the more the laboratory results are known, the better profit of them will be got. To show this potentiality, we enumerate many astrophysical applications in the certainty it will open new possibilities for astronomers not directly related with this kind of experimental work. With the purpose to approach it to them and newcomers, the main components and configuration of our experimental set up are summarized; the analysis techniques are detailed, illustrated with some examples of astrophysical relevance; and the experimental procedure is explained together with its uses and limitations to reproduce an astrophysical scenario. So, the aim of this contribution is to offer a quick look at our laboratory capabilities and to encourage astronomers to establish feasible future collaborations.

1 Introduction

There are many ways to study materials present in space: observation, theory, computational simulation and experimentation. This latter is an important mechanism to provide data to be contrasted with observations and to constrain evolutionary theories of molecules in space.

Different targets of astrophysical interest can be emulated in laboratory: gases, liquids or solid material as silicates, carbonaceous material or ices. We understand ices as the solid phase of molecules that are gases or liquids in standard

conditions; for example it is possible to produce ices of water, methane, carbon dioxide, nitrogen, etc. A particular sample prepared to imitate a particular scenario, is called “analog”. It is composed by molecules relevant for different astronomical objects as planets, satellites, comets, TNO’s in our Solar System and in the interstellar medium (ISM), see for example [1, 2, 3, 4] and the references therein. Astrochemistry and astrobiology add other types of solids to our list of analogs, organics [5, 6, 7, 8] and amino acids respectively, these latter based on results that support that they could be produced in space [9].

There are other types of astrophysical facilities, for example one devoted specifically to light scattering that has been built up at the Instituto de Astrofísica de Andalucía (IAA, Granada, Spain) by [10].

In section 2 our experimental set up is described, explaining the main components, and the procedure to do an experiment. Next sections describe each instrument we have nowadays, with references about the kind of investigations that could be performed with it, and some astrophysical applications. Results are focussed on ices; however, experiments with other species could be studied making some possible, but not always trivial, modifications to our experimental set up. The description of instruments is structured as follows: outline, uses, and astrophysical applications. Section 3 explains the possibilities of mass spectroscopy to reveal details about the ice structure. Molecular composition of a sample, and also structure, can be analyzed with infrared (IR) spectroscopy, as it is shown in section 4. The structure of ices and its variation with different parameters (i.e. temperature changes) and optical constants can be studied using UV-Vis spectroscopy (section 5). These techniques can be used before and/or after irradiation with UV photons, whose effects on ices are described in section 6.

2 Experimental set up

The goal of our experimental device is to produce results of astrophysical relevance. We want to underline that the very important thing is not to replicate the astrophysical scenario itself but the consequences of a particular process. For example it is impossible to recreate in real time scale the effect of ion irradiation on the surface of Europe [11] or in the thin ice mantle that covers the grains present in molecular clouds; therefore we must be sure we irradiate producing no additional consequences on ice (irradiation warms up) that are not naturally produced in those scenarios. None laboratory in Earth can get the conditions of pressure present in a molecular cloud, then we must be sure that the effect of pressure on the final result of an experiment is negligible. In spite of all these limitations, experimental results are crucial because the upshot of certain pro-

cesses in space can be reproduced in an appropriate experiment: UV and cosmic ray irradiation, chemical reactions, etc.

Ours, as most laboratories devoted to astrophysics in the world [60] are composed by the same basic parts:

- An experimental chamber that is a high vacuum device where pressure is controlled (pressures from several mbar down to 10^{-11} mbar are achieved).
- A controller that lets vary and/or fix the temperature from 10 K to room temperature.
- Another vacuum chamber (from now on pre-chamber) from where molecules or mixtures are supplied to the high vacuum chamber at pressures around tens of mbar. All gases or liquids must be pure, as least 99,99%.
- One or several analysis techniques. Many laboratories have in common medium infrared spectroscopy (MIR).

In our case a vacuum around 10^{-7} mbar (measured with a Hot Cathode sensor ITR 90 IONIVAC Transmitter) is obtained using a turbomolecular pump (Leybold Turbovac 50) in a High Vacuum System backed by a root pump (Leybold Trivac 16B). A compressor (Leybold Coolpack 4000) connected with a closed-cycle He cryostat (Leybold RDK 10-320) is used to cool down the sample holder to 10 K. A resistor and a temperature controller (Oxford Instruments ITC 503S) let vary up to 300 K this temperature. It must be stable when the deposition starts. It is measured with two (Scientific Instruments) silicon diodes at different locations on the sample holder, in order to control accurately the process. When desired conditions are established, the molecule (or a mixture of them) prepared in the pre-chamber passes through a needle valve to the chamber. The velocity of deposition is regulated with the aperture of this valve and the pressure in the prechamber, that is monitored with a CERAVAC CTR90. When a mixture is prepared, the proportion among gases is controlled by their partial pressures. Our sample holder, placed vertically, is a Q-sense Quartz Crystal Microbalance (QCMB) which frequency is measured precisely with a frequencymeter.

In many experiments it is important to deposit a certain thickness, for example if we want to irradiate an ice, because the penetration depth of UV photons is a fraction of microns. Thickness can be calculated in two simple ways: first, if the density is known, from measurements with the QCMB (g/cm^2); secondly, if n (the real part of the index of refraction) is known, from the interference pattern of a laser beam. Unfortunately both the density and n are usually unknown. Then it is necessary to determine both of them. We use a method called “dual-angle laser interference technique” [13]. This system allows us to determine the real part of the index of refraction of transparent non conductors and then, using

one interference pattern, obtain the thickness of the sample. Once the thickness is obtained, the density is calculated using the QCM measure.

The gas composition during deposition time is monitored with mass spectroscopy (see section 3). Once the sample is deposited, it could be characterized in our laboratory with IR spectroscopy and/or UV-Vis spectroscopy (see sections 4 and 5, respectively), or modified with UV irradiation, producing in many cases new molecules not present in the original sample (see section 6). Each molecule sublimates at certain characteristic temperature, that can vary significantly if the molecule is into a matrix of another ice (for example methane in carbon dioxide [14]). These changes can be monitored with a UV-Vis reflectance technique [1] or with mass spectroscopy in a Temperature Programmed Desorption (TPD) analysis (see references on section 3). When the temperature rises, some ices modify its structure depending on different mechanisms, see for example the best known case of water ice [15, 16, 17]. The structure of ices and mixtures is another important parameter that can be studied before and after UV irradiation (section 6), with IR and UV-Vis spectroscopy (see sections 4 and 5).

3 Mass spectrometer

The mass spectrometer is used to analyze the composition of gases present in different systems. The intrinsic characteristics of the instrument constrain the type of gases and conditions under study. In our laboratory we use a quadrupole AccuQuad Residual Gas Analyzer 100 D connected at the bottom of the vacuum chamber. With this instrument it is possible to analyze gases whose atomic weight ranges from 1 to 100 amu. The resolution is close to 0.5 amu, and it only works correctly under pressures minor than 10^{-4} mbar. This fact is not a problem because our experimental setup works usually close to 10^{-7} mbar.

The spectrometer can get a full scan of all the species present in the recipient under study whose atomic weights are into the characteristic range of the instrument. The full scan lasts around 1 minute. The result is registered as the percent in volume of every gas present in the chamber. We carry out these measurements before every experiment in order to identify gases present in our chamber and be able to detect the presence of new gases, possible contamination (atmospheric carbon dioxide and water, oil from a vacuum pump) and undesirable leaks. On the other hand, the spectrometer offers the option of selecting specific species to be scanned. In our laboratory we are interested in studying molecules of astrophysical interest (water, methane, carbon dioxide, carbon monoxide, nitrogen...). The software allows us to select the molecules to study from their atomic weight. The measured and registered magnitude is the partial pressure of each selected

gas. This last procedure, faster than that previously mentioned, makes possible to study the temporal evolution of the pressure because it takes values of pressure every few (4 or 5) seconds, when no more than 10 atomic weights are selected.

Among the parameters that we can study with the spectrometer are: porosity of ices, velocity of molecular desorption, energy of activation in the desorption process, structural changes of ices, variations of temperature desorption of molecules trapped into a matrix of different ices, etc.

The experiments performed to study the parameters listed above are known as “Temperature Programmed Desorption” (TPD) [18, 19, 20, 21, 22, 23, 24]. The procedure consists in depositing the gas (or mixture of gases) on a plate, located into the vacuum chamber previously cooled at 10 K, and then the temperature is increased at a fixed rate ($0.5 - 1 \text{ K min}^{-1}$) while the partial pressure of each gas is registered. The experiment ends when all the gases deposited sublime. There are several alternative types of experiments. For example, it is possible to initially deposit at a temperature higher than 10 K, proceed cooling the deposit down to 10 K, by finally increasing the temperature as needed.

Some porous structures could act as catalytic agents for chemical and physical processes that take place on the surface of dust grains. This fact would explain, at least partially, the rich variety of molecules present in the astrophysical environments. The experiments we plan to perform will allow us to analyze some common theories used to justify the presence of different species in planetary atmospheres.

As an example of one astrophysical application, the carbon dioxide is a gas present in the surface of different planets and satellites. The TPD experiments allow us to analyze the behaviour versus the temperature of gases like nitrogen (with a temperature of sublimation around 20 K) and/or methane (with a sublimation temperature of 40 K) trapped in the structure of carbon dioxide ices. In particular, nitrogen dominated mixtures with carbon dioxide and/or methane are relevant to studies on Triton, Pluto and Charon [14].

4 IR Spectroscopy

IR spectroscopy is commonly used to determine both the abundances and structure of molecules in a particular sample. We use a Bruker Optics IFS 66v/S series FT-IR spectrometer. It integrates a Michelson interferometer with a resolution down to 0.25 cm^{-1} . Digital Signal Processing (DSP) electronics provide full automation and precise scanner control. Spectra in the MIR ($4000-400 \text{ cm}^{-1}$ or $2.5-25 \mu\text{m}$) and FIR range ($400-100 \text{ cm}^{-1}$ or $25-100 \mu\text{m}$) can be obtained under vacuum ($< 2 \text{ mbar}$). This environment makes possible to record spectra free

from gas phase interferers, such as H₂O or CO₂, with outstanding sensitivity and stability, especially for measurements in the FIR region. For these wavelengths, the IFS 66v/S has an optional external detector port which can accommodate a liquid He cooled bolometer, permitting measurements down to 5 cm⁻¹ and a considerable increase in sensitivity (about four orders of magnitude) respect solid state detectors.

The measurements in the MIR region are performed by using the GlobarTM source, the T303 beamsplitter and the DTGS D301 detector. Measurements in the FIR region require beamsplitters and detectors depending on the sensitivity demanded by the experiment. The Multilayer T222TM beamsplitter and the DTGS D201 detector are used for low sensitivity measurements in the 400–100 cm⁻¹ (25–100 μm) range. If lower wavenumbers are required, the silicon D211 bolometer is used as a detector, the beamsplitters are the Mylar 50 and Mylar 100 μm, and the Hg Q201 lamp is the light source.

Using the A515 specular reflection unit, the IR beam is directed at right angles to the spectrometer bench, through KBr or polyethylene windows (MIR or FIR ranges respectively), where it passes through the ice film, reflects at the ice-substrate interface, and again passes through the ice film before travelling to the detector. We use this technique to obtain transmission-reflection-transmission spectra (TRT-spectra).

In space, simple molecules could be found in the form of ices on silicate or carbonaceous grain mantles in the circumstellar and interstellar medium and on solid surfaces of the outer solar system bodies and in comets. Some examples about experiments with ices and mixtures deposited at low temperatures (10 K–180 K) could be: infrared characterization [25, 26, 27]; photochemical (UV) or ion irradiation [28, 29, 30, 31]; and thermal evolution [32]. Some of the solid state species that have been reported include: H₂O, CO, CO₂, OCS, H₂CO, HCOOH, CH₄, CH₃OH, NH₃, OCN⁻, and NH₄⁺. The trend so far has been to characterize the IR bands (strength, FWHM, and peak position) mainly in the mid-infrared region where the strongest bands lie, although several studies covering the far-infrared region have also been carried out [32, 33].

The relative abundances of ice components can give key pieces of information about the chemical and physical history of the scenario in which the icy species reside. For detailed descriptions the reader is referred to [25, 27, 34]. On the other hand, UV and ion irradiation in space break bonds in the bombarded ice producing radicals that can then react to synthesize new molecules (see for example [32, 35]). As far as temperature is concerned, it has been shown by means of IR spectroscopy that the ice structure depends strongly on the thermal history [36].

To conclude the IR part of this paper, we would like to highlight the importance of carrying out laboratory experiments on the far infrared region (IR band strength and characterization, thermal annealing, etc.) in order to compare them with future data that will be obtained by the Herschel space telescope which will cover the full far infrared and sub-millimetric waveband.

5 Ultraviolet-visible spectroscopy

Traditionally UV-Vis spectroscopy has been used for obtain, for example, atomic spectra. There are other interesting applications as for example to study the structure of ices. In our laboratory we dispose of a spectrometer EPP-C 2000 from StellarNet whose specifications are: parameter value optical resolution: 0.75 nm; detector type: 2048 pixel; CCD detector range: 190-850 nm; detector integration time: 2 ms to 65 s; concave grating: Aberration corrected.

This spectrometer is able to measure spectral absorbance, transmittance, irradiance, fluorescence and emission. Transmittance and reflectance can be used to characterize fluids, gases, and optical materials. Light reflectance from solids and transmittance in fluids is also used to provide colorimetric information because the EPP-C can be used as a spectrophotometer. The instrument allows to obtain real-time spectra up to 8 wavelengths. It can replace one of the lasers of the “dual-angle laser interference technique” obtaining the second interference pattern at 633 nm. That lets us use this equipment to obtain the refraction index (within the range 190-850 nm) of films grown onto the cold (10 K) substrate [37, 38, 39, 40, 41]. This result is important by itself and because it gives us clues about the structure of the film: the value of the refraction index is related with porosity, phase (amorphous, crystalline, i.e.), density... [42, 43]. This technique is specially useful when morphological changes due to temperature variations, irradiation, etc., want to be studied. In order to evaluate them, film growth is monitored with two techniques: the double laser interferometry and UV-Vis spectroscopy. The first one gives us two interference patterns during the growth of the film and allows the measurement of the thickness as well as the refraction index at the wavelength of the lasers (at 633 nm). With these data we can fit the experimental curve, for each wavelength from the UV-Vis spectrometer, with the theoretical one obtained from the Fresnel coefficients.

6 Ultraviolet Hydrogen Lamp

It is known that interstellar ices are chemically processed by the ultraviolet (UV) radiation to form a lot of complex products. This section describes our UV lamp and some astrophysical applications.

UV photons, provided by a microwave-powered (Ophos Instruments) hydrogen lamp, are used to irradiate ice samples. This UV lamp is similar to that used by other groups [44, 45]. According to [46] the photon flux should be $\sim 10^{15}$ photons $\text{cm}^{-2}\text{s}^{-1}$ with energy $E_{\text{photons}} \geq 6$ eV [47, 48] and its spectrum is dominated by five bands at 1220 (Lyman- α), 1360, 1450, 1600, and 2800 \AA [49]. The lamp housing consists of a quartz body, mounted directly onto the sample chamber by an appropriated adapter and is separated from the vacuum by an UV-transmitting (≥ 1100 \AA) MgF_2 window whose transmission is not degraded by irradiation from high energy photons. Quartz tube (Suprasil) is fused directly to the body and it contains a mixture of 10% H and 90% Ar. The lamp runs with an Evenson cavity placed between the side arm and the enlarged portion near the front of the lamp. The discharge takes place in the central tube (diameter 12 mm, length 150 mm). Our generator is a microwave group GMP03KSM of 300 W provided by Sairem Iberica. Usually, we irradiate films with thickness of 0.1-0.2 μm , to be sure that the sample are optically thin throughout the UV range.

Molecules in the ISM suffer chemical reactions due to different processes: ionization by the interstellar radiation field, shock fronts coming from star forming regions, etc. Final result is that molecules are being destroyed and formed constantly, and observations confirm that ISM has a rich molecule chemistry. There are some models which predict this diversity of species [50] and different molecules have been identified, by means of infrared (IR) spectroscopy, as important constituents of icy grain mantles at the dense ISM. Some of them are: H_2O , CO , CH_3OH , H_2CO , CH_4 and CO_2 [51, 52, 53].

Our laboratory studies are relevant mainly for three reasons. First of all, they can help to understand the composition and evolution of interstellar ices. Secondly, the UV photolysis may be an important agent in modifying species because it could explain why we can find specific species in some “impossible” conditions, as a result of cycles of desorption and accretion processes [54, 55, 50]. And finally, it can also explain the possibility to form complex organic species from simple ices, as it occurs in the diffuse ISM, in cometary dust, etc. [56, 57, 58, 59].

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