

IR PROPERTIES OF ASTROPHYSICAL ICES IN THE UNIVERSE

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Abstract: Part of our knowledge about interstellar, planetary and cometary ices derives from the identification of bands in astronomical spectra of distant objects, rather than from direct measurement. Therefore, laboratory experiments on simple ices and its mixtures carried out under physical conditions as close as possible to the astrophysical environments are essential for the identification of ices present in space.

In this work, we first give the reader an introduction to the infrared properties of the ices present in the Universe, defining the term ice and showing the importance of infrared spectroscopy for the study of ices, the locations in space where ices are mainly found along with the ices detected so far, and some of the experimental laboratories around the world working on ice studies.

The second part of this work is focused on the Experimental Astrophysics Laboratory we have set up in order to characterize in the mid and far infrared range (MIR and FIR respectively), which covers the 2.5-1000 μm region, ices of astrophysical interest. One of the key components of the laboratory is a Si composite bolometer cooled by liquid He used to obtain spectra with a sensitivity much greater than that obtained with a standard DTGS detector working at room temperature in the FIR where bands of small intensity lie. The MIR and FIR spectra we shall obtain in the future will serve to characterize in those spectral ranges some simple ices and their mixtures and also to compare data mainly coming from the forthcoming Herschel satellite with laboratory data. It is also planned to do a systematic laboratory study of the effects that ultraviolet (UV) photolysis and temperature have on the ice band profiles and on the ice structure.

Keywords: Ices – Infrared Spectroscopy – Laboratory Experiments – Interstellar Medium – Solar System.

1 Introduction

Astronomy studies the properties of the radiation (light) reaching us from celestial objects. Cool objects – up to temperatures of 3500 °C – radiate most of their energy at infrared (IR) wavelengths while hotter objects like the Sun radiate strongly at shorter wavelengths. The cool Universe is therefore best studied in the IR region. The Universe is full of cool objects, such as planets, dust and ageing stars, none of which generally shine brightly in the optical part of the spectrum. In fact, observations of these objects began with the arrival of sensitive IR detectors [1]. The first IR observations with a space-based telescope were carried out by the Infrared Astronomical Satellite (IRAS) [2]. Twelve years later, the Infrared Space Observatory (ISO) was launched [3]. Currently, the Spitzer Space Telescope [4] and the AKARI mission [5] are making an all-sky survey obtaining spectra of much better sensitivity than the previous ones. On the other hand, these missions are all limited to wavelengths below 200 μm . Nevertheless, the upcoming Herschel Space Observatory (HERSCHEL) [6] will provide spectra of high spectral resolution from 55 to 672 μm covering the far infrared and submillimetre spectral range.

Each substance produces a different spectrum which can therefore be used as an identifier. IR spectra are one of the tools used to extract great amount of information from objects in the Universe. Some bands (features) of these IR spectra are caused by species in the form of ices.

A good understanding of the term “ice” is needed. The term ice typically refers to a solid composed of molecules which form a gas or a liquid at 25 °C and 1 bar. A distinction between a one-component and a multi-component solid is also needed. With this purpose expressions such as “pure ice” and “mixed-molecular ice” can be employed, respectively [7].

Ices absorb specific wavelengths of light at IR frequencies depending on their molecular bonding and composition. The mid-infrared region (4000–400 cm^{-1} or 2.5–25 μm) contains the infrared active fundamental bands (intramolecular vibrations) as well as some low order overtone and combination modes [8]. The broad absorptions in the far infrared region (400–10 cm^{-1} or 25–1000 μm) are due to lattice modes (intermolecular vibrations) [9]. Moreover, ice bands can be distinguished from bands of gas phase molecules because ice bands lack the characteristic ro-vibrational structure of gases and are shifted and broader.

One of the scenarios where ices are thought to be present is on the surface of dust grains in the interstellar and circumstellar medium [10]. In fact, ices are generally one of the major components of the cold clouds in the interstellar medium and show large variations in abundances and profiles which means they can be used as powerful diagnostics of changes in astrophysical environments. Some bodies in the Solar System where ices have been reported are the surfaces of some planets and satellites, some small bodies – comet nuclei, Trans-Neptunian Objects (TNOs), centaurs– and even

some planetary rings [11] and some comet tails [12]. On the other hand, comets are considered to be the most primitive objects in the Solar System. The composition and structure of their nuclei contain a record of the primordial solar nebula at the time of its formation. Cometary nuclei are made of refractory solids and frozen volatiles. Moreover, the composition of volatiles is thought to be similar to that observed in dense molecular clouds. It therefore seems that there is a close relationship between cometary materials and interstellar icy grain mantles [7].

Dust grains are microscopic particles whose sizes are usually less than 1 micrometre. These grains are represented by a core of refractory materials (silicates, amorphous carbon, and organic residues) covered with an icy mantle largely dominated by H₂O ice but also with other major components as CO, CO₂, NH₃, CH₃OH, and H₂CO ices. The visible light wavelength is of the same size of many dust particles, consequently the visible light is scattered by the dust; however, longer wavelengths such as IR radiation passes through. On the other hand, the dust itself is also a source of IR radiation that can be picked up by detectors. For instance, stars, depending on their temperature, emit in a particular range and it is possible to detect their absorbing spectra. Besides, this starlight may be absorbed by the surrounding dust grains which will be warmed up and start to radiate in the IR wavelength. This absorption of energetic radiation and reemission at less energetic wavelengths is very efficient and dust clouds emit the majority of their energy at IR wavelengths. A similar situation occurs with dust grains of cometary tails when they are approaching the Sun.

In the website of the Cosmic Ice Laboratory at NASA's Goddard Space Flight Center [13] we can find listed the Solar System ices and also the detected molecules in the interstellar medium and in comets. Some of the molecules of the interstellar medium have been identified in their ice phase as well as their gas phase (e.g. H₂O, CO, CO₂, OCS, NH₃, CH₄, CH₃OH). On the other hand, the existence of a great number of molecules in gas phase—some of them with a high number of atoms (e.g. benzene)—is significant; in fact it indicates that a rich chemical activity is taking place inside these environments. There is also in this website a database containing MIR and FIR reference ice spectra. Other research groups have also carried out ice spectroscopy applied to different astrophysical environments, namely, the Leiden Molecular Astrophysics group in Holland [14], the Experimental Astrophysics Laboratory group at Catania in Italy [15], the NASA Ames Research Center group in USA [16], the Laboratory Astrophysics Facility group at University College in Australia [17], and the Laboratory for Atomic and Surface Physics at Virginia in USA [18]. Among all these groups, the Cosmic Ice Laboratory at NASA's Goddard Space Flight Center, the Laboratory Astrophysics Facility at University College, and the NASA Ames Research Center group have carried out ice spectroscopy in the FIR up to 100, 110, and 200 μm , respectively.

The abundance of different ices depends on the astrophysical environment. H₂O ice is clearly dominant in almost all these environments. In the case of Solar System

bodies where the ices are found mainly on the surfaces of the bodies, most of the identified surface ices consist primarily of water. Some exceptions are the surfaces of Triton and Pluto which are covered with carbon and nitrogen containing ices and the surface of Io which is dominated by sulphur containing ices. In the case of interstellar ices, in addition to the H₂O ice, other major ice components are CO, NH₃, CH₃OH, CO₂ and H₂CO. In the case of cometary nuclei the composition of the volatile ices is largely dominated by H₂O ice (about 70–90%) while other major ice components are CO, CH₃OH, CO₂, and H₂CO. The similarity between the volatile ices in comets and interstellar ices tends to support a close relationship between cometary materials and interstellar icy grain mantles. Thus, cometary ices constitute a link between interstellar and Solar System materials [19, 20, 21].

As said previously, ices in the interstellar and circumstellar medium are detected on silicatic and carbonaceous grain mantles. In the formation and evolution of those ices a number of different processes play a role. In fact, the ices can be formed by sublimation and recondensation after being synthesized on grain surfaces or directly frozen from gas phase as in the case of CO. However, other more energetic ways of ice synthesis are also possible such as UV photolysis, ion irradiation and thermal annealing. The Solar System and cometary ices are also subjected to radiation processing coming from the magnetospheres, cosmic rays, solar wind and flares, and solar UV field. The effect that energetic charged particle irradiation and UV photolysis have on the ices is that when an energetic ion or UV photon collides with the ice, part of the deposited energy destroys bonds in the target, forming radicals that can then react to synthesize new molecules. In this way, new molecules are produced by irradiation being an example of this phenomenon the hydrogen peroxide molecule which has been detected on the surface of the Galilean satellite Europa, whose surface is being bombarded by ions coming from the intense Jupiter magnetosphere [22]. Temperature variations in astrophysical scenarios may alter the ice phase producing a phase change via amorphization or crystallization. To study the role played by each of the latter processes in ice evolution, different groups are carrying out laboratory experiments simulating the astrophysical scenario under study. In this way, experiments such as UV photolysis [23, 24, 25, 26, 27], ion irradiation (radiolysis, e.g., [28, 29, 30, 31, 32, 33]) and surface chemistry [34, 35] provide us with information about the basic processes of ice formation, adsorption, desorption, diffusion, and even reaction pathways.

Lastly, laboratory experiments can shed some light on, for example, how the intrinsic strength of each band depends on the chemical environment of the molecule, or how the position of the stretching mode shifts by 20 cm⁻¹ and its width broadens by a factor of two when the CO₂ is mixed with H₂O ice rather than in its pure form, or how the ice profile of crystalline material can be distinguished from their amorphous counterparts by being sharper and red-shifted and, finally, how to analyze the band profiles making studies with layered ices, in which some molecules (e.g., CO) are not

mixed with H₂O [36]. In other words, laboratory experiments on simple ices and their mixtures carried out under physical conditions as close as possible to the astrophysical environments are essential to provide the basic data to analyze quantitatively the ice bands (e.g. [37, 38, 39, 40])

2 Description of the Experimental Astrophysics Laboratory

2.1 Experimental equipment

Our astrophysics laboratory located at the Escuela Politécnica Superior de Alcoy (Valencia, Spain) is composed of several basic parts. The main one is an experimental chamber that is a high vacuum device where a pressure of 10^{-7} mbar is obtained using a turbomolecular pump in a High Vacuum System backed by a root pump. A compressor connected with a closed-cycle helium cryostat is used to cool the sample down to 10 K. A resistor and a temperature controller permit varying the temperature up to 300 K. This temperature is measured with two silicon diodes at different locations on the sample holder. The gas molecules or a mixture of them prepared in a pre-chamber pass through a needle valve to the chamber when the proper conditions are reached. The velocity of deposition is controlled and regulated by the aperture of this valve and the pressure in the pre-chamber. The proportion among the gases is controlled by their partial pressure measured with a ceramic sensor not influenced by the gas type. The sample holder is a Q-sense Quartz Crystal Microbalance (QCMB) whose frequency is measured precisely with a frequency meter.

The second part is a mass spectrometer which is used to analyze the composition of the gases. This spectrometer is connected at the bottom of the vacuum chamber getting a full scan of all the species present in the chamber. The result is registered as the percentage in volume of every gas present. The spectrometer also offers the option of selecting specific species to be scanned being the measured and registered magnitude the partial pressure. Because the spectrometer takes pressure values every 4 or 5 seconds, it is possible to study the temporal evolution of these pressures.

The third part is an ultraviolet Hydrogen lamp that provides ultraviolet (UV) photons, which are used to irradiate the ice sample. The photon flux should be about 10^{15} photons $\text{cm}^{-2} \text{s}^{-1}$ with energy $E_{\text{photons}} \geq 6$ eV and its spectrum is dominated by five bands. We usually irradiate ice films with a thickness of 0.1–0.2 μm to be sure that the sample is optically thin. This irradiation destroys and produces new species which can be detected in different ways. However, they are very well observed with IR spectroscopy.

The fourth part is the IR spectrometer, a Fast Fourier Bruker IFS 66v/S, which integrates a Michelson interferometer obtaining spectra with a resolution better than

0.25 cm^{-1} . The spectrometer operates under vacuum conditions of 10^{-1} mbar in the optics and the sample compartment. This environment makes it possible to record spectra free from gas phase interference such as H_2O or CO_2 in the MIR and especially for measurements in the FIR where water vapor contamination is very pronounced. The basic components of a spectrometer are the source, the beamsplitter and the detector. These components must be selected depending on the spectral range under study; in our particular case the MIR and the FIR. We are equipped with the Globar and the Hg-Arc sources, for the MIR and FIR, respectively and with a KBr beamsplitter for the MIR and four Mylar beamsplitters (6, 25, 50 and $100\ \mu\text{m}$) covering all the FIR range. Concerning the detectors we have two DTGS (deuterated triglycine sulfate) for the MIR and the FIR, respectively, and a Si bolometer -a very high sensitivity detector- covering the spectral range $670\text{--}10\text{ cm}^{-1}$ ($15\text{--}1000\ \mu\text{m}$). The two greatest disadvantages of the DTGS detectors are their low sensitivity and their slowness. On the other hand, the Si bolometer allows measurements of high sensitivity in much shorter time. Nevertheless, this detector must be cooled with liquid helium and its dewar pre-cooled and refrigerated with liquid nitrogen being its use quite complex. Moreover, liquid helium is very expensive and evaporates quickly which implies that the experiments must be well planned.



Figure 1: The spectrometer, the 3D movable high vacuum chamber, the silicon bolometer and the helium container

Figure 1 is showing the experimental configuration designed by us in order to obtain IR spectra of simple ices and its mixtures in the MIR and FIR. This configuration integrates the IR spectrometer, the high vacuum chamber and the Si bolometer

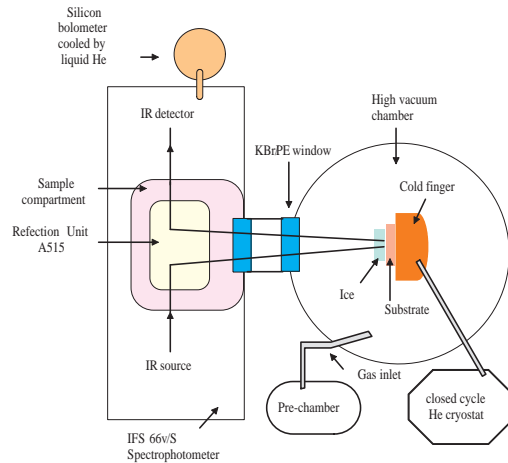


Figure 2: Block diagram showing the IR spectrometer, the bolometer and the high vacuum chamber

together. In order to offer the possibility of carrying out several experiments on the same sample at the same time the high vacuum chamber is located outside the sample compartment of the IR spectrometer making the four chamber's windows available. An essential part of this design is a mechanism that allows us to move the high vacuum chamber in the three spatial dimensions by using a micrometric adjustment, which allows the right alignment of the IR beam when it travels from the IR source to the detector.

Figure 2 shows a bottom view of our design, the IR spectrometer on the left and the high vacuum chamber on the right. The technique we are using to obtain measurements is the TRT (Transmission-Reflection-Transmission). The beam is directed to the cold finger in the chamber by using the reflection module A515. There is a vacuum of 10^{-1} and of 10^{-7} mbar inside the interferometer sample compartment and the ice chamber, respectively. In order to solve the problem with the vacuum, when the beam is traveling outside and between the interferometer and the ice chamber, we use nitrogen gas. As the high vacuum chamber is located outside the interferometer sample compartment forces it to work in TRT. However, this fact allows us to carry out different experiments at the same time on the same ice sample. We are considering this possibility because it can give complementary information about the same ice sample. A modification of the high vacuum chamber is being done; specifically two quartz crystal microbalances covered by their respective plane optically thick gold films have been placed on both sides of the cold finger in a way that simultaneous

gas depositions take place.

Finally, in our laboratory we also use a UV-Visible spectrometer EPP-C 2000 from Stellar.net.

2.2 Measurements carried out

Bellow, we describe the experiments we are carrying out at the present time. We have measured the density and the index of refraction real part of simple ices (e.g. CH₄, N₂ and CO₂) and their mixtures at low pressure ($P < 10^{-7}$ mbar) and at temperatures ranging from 10 K up to the sublimation temperature of the species or mixture under study [41]. The technique used has been double laser interferometry. There is a lack of density measurements for ices other than water at the low temperatures and pressures found in space environments and cryogenic laboratory systems. Moreover, the density is related with the porosity which is another useful parameter to characterize the ice structure. By knowing how the ice density varies with temperature some clues can be obtained about structural changes as a function of temperature. In order to obtain the real part of the refractive index in the UV-Visible range (200–800 nm), we use a UV-Visible lamp which is directed to the growing ice. The reflected beam is collected by a UV-Visible spectrometer and we can draw an interference curve each 0.2 nm in this range, that allows the calculation of the refractive index value [42].

We have also conducted some experiments on temperature desorption at a constant warming up rate. In particular, the ability of CO₂ ices to trap other gases such as CH₄ [43] has been studied. These kinds of studies are necessary to better understand the processes that occur in the surfaces of some Solar System bodies as in the case of Triton where ices of N₂, CH₄, CO, CO₂, and H₂O are present on its surface. In particular, the process of ice trapping in some ice matrix explains the fact that the trapped ice sublimates at higher temperature than usual.

Some experiments on UV irradiation of simple ices and its mixtures have also been carried out [44]. We have verified that CO₂ ice irradiation produces CO ice. As previously stated, UV irradiation produces new molecules originally not present in the target. At this moment, these new molecules have been detected by mass spectrometry although we have planned in the near future to use the IR spectrophotometer to characterize the new species by means of their IR absorption bands.

2.3 Measurements planned in the future

One of the aims of our laboratory in the forthcoming years will be to obtain high sensitivity spectra of molecular ices and their mixtures in the MIR and the FIR up to 670 μm [45]. We plan to obtain the ice band profiles, peak positions, and FWHM as a function of temperature. By depositing the ices at different temperatures the

amorphous and crystalline phases of the ices will be obtained and characterized. Phase change studies will be another type of experiments that are scheduled.

In addition, with the design presented above we will focus on carrying out several experiments at the same time on the same sample by using techniques such as IR spectroscopy, UV irradiation, temperature desorption, UV-Visible spectroscopy, etc. [45].

3 Conclusions

In this work, we have presented an introduction to the infrared properties of ices in the Universe. The places in the Universe where ices are mainly found have been described both in the Solar System and in the interstellar medium. In addition, the astrophysical processes which determine the evolution of the ices (temperature changes, ionizing irradiation, adsorption and desorption processes, etc.) have been mentioned. At the Department of Applied Physics of The University of Valencia at Alcoi (Spain), we have set up an Experimental Astrophysics Laboratory to simulate the formation and subsequent processing of ices in space. Our main goal is to characterize simple ices and their mixtures. Currently, we are able to carry out experiments on UV irradiation, temperature desorption, UV-Visible spectroscopy, density measurements, and to obtain the index of refraction real part of ices and their mixtures. In the future, we plan to obtain IR spectra in the 2.5-670 μm range of simple ices and their mixtures of astrophysical interest in order to compare laboratory data with spatial data coming from the forthcoming Herschel mission.

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