

The Interstellar Astrochemistry Chamber (ISAC)

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The Interstellar Astrochemistry Chamber (ISAC) is mainly designed for the study of solids (ice mantles, organics, and silicates) in interstellar and circumstellar environments: characterization of their physico-chemical properties and their evolution due to vacuum-UV and/or cosmic ray irradiation, and thermal processing.

ISAC is an ultra high vacuum chamber, with base pressure down to $P = 2.5 \cdot 10^{-11}$ mbar, where an ice layer made by deposition of a gas mixture onto a cold finger at 10 K, achieved by means of a closed-cycle helium cryostat, can be irradiated with UV photons. We intend to incorporate also an ionic source for the simulation of cosmic ray processing. Samples can be heated in a controlled way from 10 K to room temperature. The evolution of the solid sample is monitored by in situ transmittance FTIR and Raman spectroscopy, while the volatile species are monitored by QMS. Gas mixtures typically contain H₂O and CH₃OH vapors, mixed with gases like CO, CO₂ and NH₃. The gas line works dynamically, and allows the deposition of gas mixtures with the desired composition, that is monitored in real time by a QMS. A prechamber is used to introduce and extract the samples preserving the ultra high vacuum in the main chamber.

Some experiments for the calibration of ISAC are presented.

Keywords: Methods: laboratory – ISM: molecules, dust, extinction – Infrared: ISM Techniques: spectroscopic

1. Introduction

Mineral and carbonaceous grains, present in the atmospheres of giant stars, are ejected into the interstellar medium (ISM). Dust grains in the diffuse ISM (hydrogen number density lower than 10^3 cm^{-3}) have typical sizes of tenths of micron with individual masses of the order of 10^{-14} - 10^{-12} grams. They experience a UV photon field of $\approx 8 \cdot 10^7$ UV photons $\text{cm}^{-2} \text{ s}^{-1}$ with photon energy $E_{\text{ph}} \geq 6 \text{ eV}^1$ and cosmic ray irradiation, mainly due to protons of MeV energies and electrons, and partly also to heavier ions.² As a result of such irradiation the typical temperature of dust in the diffuse medium is around 100 K. The main components of dust observed in the diffuse ISM, as inferred from infrared observations, are highly amorphous silicates (responsible for the 10 and 18 μm absorption bands) and a form of hydrogenated amorphous carbon (responsible for the 3.4 μm feature).

Dense molecular clouds in the ISM (typical densities of 10^4 cm^{-3}) have temperatures as low as 10 K in the interior due to shielding from UV irradiation. Here dust particles like those present in the diffuse medium accrete ice mantles, with estimated thicknesses of hundredths of micron, composed mainly of H_2O , and other species like CO, CH_3OH , CO_2 , and NH_3 .³ Icy dust particles in dense clouds are submitted to energetic processing, mainly by the cosmic-ray induced UV field, and partly by direct energy input by cosmic-ray particles of 1-1000 MeV energies. The energy deposition increases as the energy of the particle decreases and therefore 1 MeV protons are the most relevant.² Young stars are born in dense clouds, the envelopes around stars contain icy grain mantles similar in composition to those present in dense clouds.^{4,5} Such circumstellar ices will be exposed to irradiation from the central star and the surrounding diffuse ISM, providing a new scenario for energetic ice processing.⁶ These envelopes often give rise to disks, which in turn can lead to planetary systems. The evolution of the solar nebula led to the formation of planets, comets, and asteroids.

The first laboratory dedicated to the simulation of energetic processing of interstellar dust was founded in the Leiden Observatory by J. Mayo Greenberg and Lou J. Allamandola in the mid-seventies. The experimental system in Leiden was adapted by L. Allamandola in NASA-Ames, and later by L. d'Hendecourt at the IAS in Orsay. The typical experimental system consists of a high vacuum chamber with a pressure of the order of 10^{-7} mbar, where an ice layer is formed at 10 K, which can be irradiated with vacuum UV light (groups at NASA-Ames, IAS in Orsay, CIA in Alcoa, University of Virginia, Hokkaido University, etc.), vacuum/extreme UV light using synchrotron radiation sources (University of Southern Cal-

ifornia, National Central University in Taiwan), or ions (groups at NASA Goddard Space Flight Center, Osservatorio di Astrofisica di Catania, Osservatorio Astronomico di Capodimonte in Naples, etc.). In recent years, some experiments were performed combining both photons and ions (NASA Goddard Space Flight Center and Osservatorio di Astrofisica di Catania). In situ analysis of ice is generally performed by Fourier Transform Infrared (FTIR) spectroscopy, but the Osservatorio di Astrofisica di Catania team has successfully used a Raman spectrometer. Some laboratories are now using ultra-high-vacuum (UHV) systems for ice UV-irradiation experiments, e.g. the Sackler laboratory from Leiden Observatory.

In the last years, three laboratories dedicated to study astrophysical ices were established in Spain. These are the CIA in Alcoy (Politechnical University of Valencia), the group at the IEM (CSIC) in Madrid, and the group at CAB (CSIC-INTA) in Torrejón de Ardoz (Madrid). The Interstellar Astrochemistry Chamber (ISAC), located at CAB, is mainly designed for the study of solids (ice mantles, organics, and silicates) in interstellar and circumstellar environments: characterization of their physico-chemical properties and their evolution due to vacuum-UV and/or cosmic ray irradiation, and thermal processing.

The density on the surface of the Earth at sea level is about 3×10^{19} molecules cm^{-3} , corresponding to 1 bar. Thus, at room temperature, a rough estimate of the pressure in the dense interstellar medium, with densities of 10^3 – 10^6 particles cm^{-3} , is between 10^{-14} and 10^{-10} mbar.

This paper describes the ISAC setup and the experimental protocol. It reports some data obtained during the calibration of the system. ISAC is essentially an UHV chamber, with pressure typically in the range $P = 2.5$ – 4.0×10^{-11} mbar, where an ice layer made by deposition of a gas mixture onto a cold finger at 10 K, achieved by means of a closed-cycle helium cryostat, can be UV irradiated. Samples can be heated from 10 K to room temperature. The evolution of the solid sample is monitored by in situ transmittance FTIR and Raman spectroscopy, while the volatile species are monitored by quadrupole mass spectroscopy (QMS). Gas mixtures typically contain H_2O and CH_3OH vapors, mixed with gases like CO , CO_2 and CH_4 . The gas line works dynamically, and allows the deposition of gas mixtures with the desired composition, that is monitored in real time by QMS. There is a second deposition tube for co-deposition of corrosive gases, like NH_3 . A prechamber is used to extract the samples preserving the UHV in the main chamber.

Probably the outstanding characteristics of ISAC, compared to other

systems, are the excellent UHV conditions with pressures down to $2.5 \cdot 10^{-11}$ mbar after baking the system, the prechamber for the extraction of samples with no need to break the UHV of the main chamber, and the novel design of the gas line system for the preparation of complex gas mixtures with unprecedented accuracy in the composition. In addition to FTIR spectroscopy, we plan to perform Raman spectroscopy in the near future, and to incorporate an ion source for simultaneous irradiation of the ice with photons and ions.

2. Technical description of ISAC

A cartoon image of ISAC is shown on Fig. 1. The setup has a vertical configuration, consisting of two chambers: the main chamber, where gas deposition onto a substrate located at the tip of a cryostat (cold finger), and irradiation of the formed ice layer takes place, and a prechamber separated by a valve from the main chamber. The prechamber allows the introduction and extraction of samples with no need to break the vacuum in the main chamber. The main chamber has two levels. The sample holder with the substrate, usually an infrared transparent window, placed at the cold finger, is at the upper level, where it is intersected by the beam of the FTIR spectrometer and irradiated by the UV lamp (an ion source and a UV-spectrophotometer will be implemented in the future). There is also a QMS at the upper level for monitoring of the volatiles. An schematic view of the upper level is shown on Fig. 2, with the sample holder at the deposition position. Rotation of the sample holder by 90° is required for FTIR spectrometry of the sample. The lower level is where the pumps are located, as well as the two gas deposition tubes, the pressuremeters and the Raman spectrometer. As mentioned above, the base pressure at room temperature in the main chamber is $2.5\text{--}4 \cdot 10^{-11}$ mbar, thanks to the combination of a series of UHV pumps. The samples can be cooled down to 10 K and warmed up to room temperature thanks to a closed-cycle helium cryostat and a tunable heater, that in combination with the QMS of the main chamber, allows temperature programmed desorption (TPD) experiments on ices.

A gas line monitored by a second QMS is attached to the main chamber for controlled deposition through the deposition tubes. The gas line consists of a novel design that allows the preparation of gas mixtures containing up to 5 different species. The ISAC setup components are described in more detail below.

- **Prechamber for sample introduction:** A small chamber is on

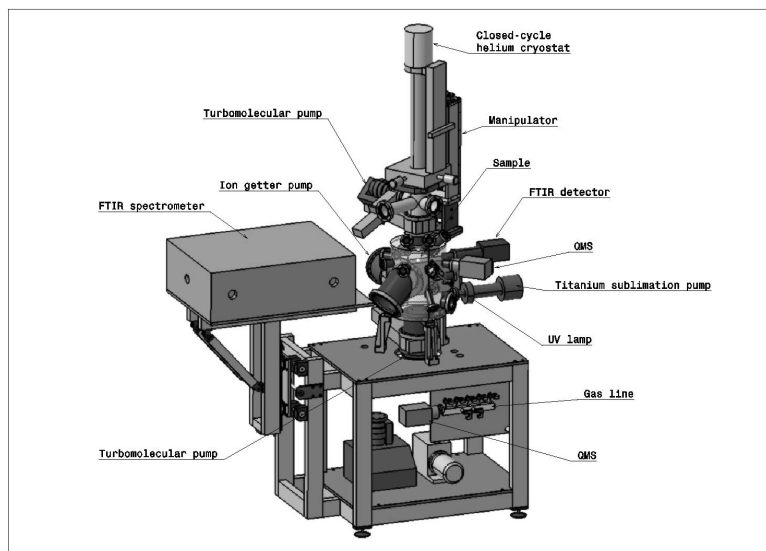


Fig. 1. Schematic cartoon of the ISAC experimental setup.

top of the main chamber separated by a hydraulic VAT valve. The samples are introduced and extracted from the system via the prechamber. This is done by vertical translational movement of the cold finger, where the sample holder is located. The prechamber is practical because it makes the work easier and it shortens the time between experiments from three to one day, thus enhancing the durability of the vacuum components and optimising the system performance. It consists of:

- Fast entry lock.
- Pumping system: Independent from that of the main chamber, which reaches a pressure of about 10^{-9} mbar. It supports the pumping system of the main chamber when the valve connecting the two chambers is open. It consists of a turbomolecular pump (abbreviated TMP) backed up by a rotary pump, and a titanium sublimation pump (TSP).

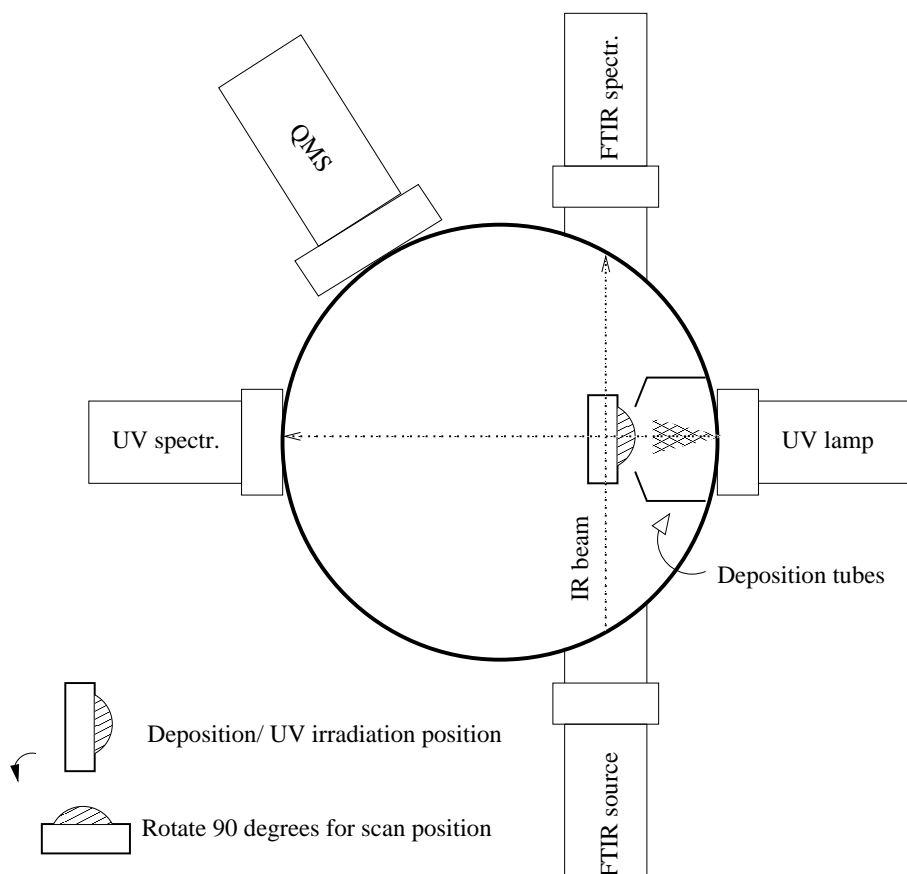


Fig. 2. Schematic representation of the upper level of the main chamber of the ISAC experimental setup, where gas deposition onto the cold substrate forms an ice layer that is UV irradiated. FTIR and QMS techniques allow in situ monitoring of the solid and gas phases.

- Cold finger with sample holder connected to a closed-cycle-He-cryostat by a gold ring. The sample holder is mounted on a tube that can be rotated by 360° and moved translationally to place samples in the main chamber. The temperature range is between 10 K and 400 K at the sample position.
- **Main chamber:** where ice deposition and irradiation takes place. The interior of the chamber is covered by Mu-metal in order to isolate it from external magnetic fields. The UV lamp is positioned

in front of the deposition substrate so that the sample is irradiated homogeneously. A cylindrical quartz tube of 10 mm diameter, placed between the lamp and the sample holder, acts as an optical guide to maximize the flux, given in UV photons $\text{cm}^{-2} \text{s}^{-1}$, at the sample position. A UV spectrophotometer will be mounted on the opposite side of the main chamber to allow in situ monitoring of the UV flux. A Bayer-Alpert pressuremeter measures pressures in the 10^{-11} mbar range. The characteristics of the deposition or main chamber are:

- **Pumping system:** The combination of a series of UHV pumps is aimed to obtain a base pressure down to $\sim 2 \cdot 10^{-11}$ mbar. It consists of:
 - * TMP of 550 l/s with connection flange DN 160CF and integrated controller. Pumping capacity of H_2 :450 l/s, He:520 l/s, N_2 :510 l/s, Ar:500 l/s. The pump is backed up by a second TMP and a rotary pump.
 - * TSP.
 - * Non-Evaporable Ion Getter (IGP) pump.
- **Vacuum UV lamp:** The UV source is a microwave stimulated hydrogen flow discharge lamp (output $1.5 \cdot 10^{15}$ photons s^{-1} , $E_{\text{photon}} = 7.3\text{-}10.5$ eV), purchased from Ophos, which is separated from the vacuum chamber by a MgF_2 window. Using the x-y manipulator, the sample holder can be positioned in close contact to the quartz tube acting as an optical guide. That way, the circular spot size of the UV flux at the sample position has a diameter slightly larger than the 10 mm diameter of the quartz tube, which corresponds roughly to the size of the 13 mm diameter infrared transparent window where ice deposition takes place. The UV lamp requires a simple circuit where hydrogen circulates from a hydrogen bottle to the lamp and it is pumped by a roughing pump. A microwave generator with a 100 W power is responsible for the excitation of the hydrogen. The Evenson cavity of the lamp is refrigerated with air. The UV photon spectrum of this hydrogen-lamp resem-

bles that of the diffuse interstellar UV field.^{6,7}

- **Analytical techniques:** provide the in situ characterization of the samples during the deposition/irradiation and warmup. Fourier-transform infrared (FTIR) spectroscopy provides the ice composition and aids the characterization of the more refractory products observed at room temperature. Due to the different selection and excitation rules, Raman spectroscopy allows the detection, general characterization and determination of the structure of organic matter, even at cryogenic temperatures. The quadrupole mass spectrometer (QMS) provides the in situ detection of volatiles produced during warmup of the ice and serves to control the gas deposition. An UV spectroradiometer will be installed to monitor the UV flux of the lamp.
 - * **FTIR spectrometry:** It is done in transmittance, using a Vertex 70 Bruker spectrometer, equipped with a DTGS detector working in the 7500 to 370 cm^{-1} (~ 1.3 to $27\text{ }\mu\text{m}$) spectral range. The main vibrational molecular modes are commonly observed in that range. The infrared beam goes across the main chamber through two ZnSe windows.
 - * **Raman spectrometry:** A HORIBA Jobin Yvon iHR550 spectrometer will be used. The laser wavelength is 532 nm (green). The laser makes an angle of 45° with the deposition window.
 - * **Quadrupole mass spectrometry (QMS):** Pfeiffer Prisma with mass spectral range from 1 to 100 amu . Serves for the detection of molecules ejected from the ice surface into the gas phase and to measure the residual gas composition. It is also used to monitor the deposition.
- **Gas line:** For the preparation of gas mixtures for deposition. A mixture of a maximum of 5 components can be prepared in the gas line. The design of a gas line for the preparation of a complex gas mixture under controlled conditions, containing H_2O and CH_3OH vapor and three gas components,

commonly CO, CO₂, and CH₄, was an important challenge. This was accomplished using electrical valves to control the entrance of the individual components and working dynamically at a total pressure below 1 mbar, thus ensuring laminar flow conditions. The electrical valves are activated according to the partial pressures measured by a QMS, that is connected to the gas line. Either CH₃OH or H₂O are deposited manually into the gas line, and the other components are deposited proportionally to the amount of CH₃OH/H₂O in the gas line. The QMS monitors the composition of the gas mixture at any time. When the desired composition of the gas mixture is obtained, the deposition tube is opened through a needle valve and the gas enters the main system, accreting onto the substrate window at 10 K and forming an ice layer. In addition, there is a second deposition tube for the deposition of corrosive gases, like NH₃, into the main chamber.

3. Experimental protocol

The experimental protocol that is described below corresponds to a deposition/irradiation experiment for the simulation of icy grain mantle processing in the interstellar/circumstellar medium. It comprises the following steps:

- In the prechamber compartment, while the valve between the prechamber and the main chamber is closed, an infrared transparent window (CsI or KBr) is fixed on the tip of the cryostat. The infrared window serves as the substrate for the deposition. Afterwards, the fast entry lock is closed and the prechamber is evacuated.
- Once the vacuum in the prechamber is of the order of 10^{-9} mbar, the valve connecting the prechamber to the main chamber is opened. The base pressure in the main chamber should be below $4 \cdot 10^{-11}$ mbar and the cryostat is moved downwards so that the substrate is on the deposition/irradiation position.
- A gas mixture for deposition is prepared in the gas line. Predeposition is started, with the substrate at room temperature, to calibrate

the flow of the deposition and set the valve positions that correspond to the desired gas flow. The Langmuir relation provides an approximation of the number of monolayers of ice deposited as a function of the pressure of the gas and the deposition time, assuming a sticking coefficient equal to unity, which is valid for cryogenic temperatures around 10 K. One Langmuir (1 L) corresponds to the deposition of one monolayer, and it is given by $1 \text{ L} = 10^{-6} \text{ Torr s}$.

- The cryostat is turned on and the temperature reaches $\approx 10 \text{ K}$. The valve connecting the gas line with the main chamber is opened, at the position determined during the predeposition, to start the deposition. During the deposition the ice layer can be irradiated with photons and/or ions. At different intervals, the cryostat can be rotated 90° to perform transmittance FTIR spectroscopy, to monitor the ice evolution. Raman spectroscopy can be done at the deposition/irradiation position of the sample. QMS monitors the gas phase molecules during the deposition and irradiation.
- Once the deposition/irradiation is completed, the warmup can be started following a linear heating ramp of 1 K min^{-1} or lower. QMS is used for the detection of volatiles during warmup, while FTIR and Raman spectroscopy are employed to monitor changes in the ice composition and structure.
- At room temperature, the cryostat is pulled up, the substrate with the refractory organic residue is now in the prechamber, which is isolated from the main chamber closing the VAT valve, so that the sample can be extracted from the setup without breaking the vacuum in the main chamber. The organic residue, obtained from irradiation and warmup of the interstellar/circumstellar ice analog, can be analyzed ex situ by other techniques.

4. Calibration experiments

Fig. 3 shows the mass spectrum of the residual gas in the main chamber of ISAC, measured at a pressure of $3.6 \cdot 10^{-11} \text{ mbar}$. Under those UHV conditions the dominant gas component is H_2 , see figure caption. A simple test can be carried out to observe the pumping efficiencies of the pumps. Fig. 4 illustrates the role played by the different pumping systems in the

10^{-11} mbar total gas pressure range. The partial pressures of H_2 , H_2O , and CO increase significantly when the valve connecting the IGP to the main chamber is closed, and rapidly reach their initial values when the valve is opened again, showing that those gas components are continuously pumped by the IGP. Only H_2 is clearly pumped continuously by the TSP, albeit less efficiently than the IGP. H_2 , CO , Ar , and CH_4 gas molecules are pumped continuously by the TMP. Except for eventual jumps during valve opening/closing, likely due to retained pockets of gas, the partial pressures of CH_3OH , O_2 , and CO_2 do not vary much, indicating that those species have reached their minimum partial pressure values.

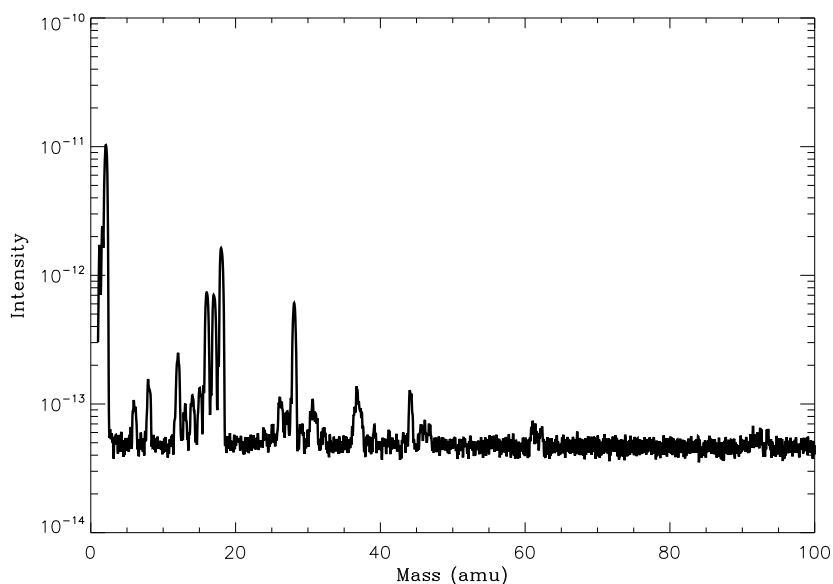


Fig. 3. Residual gas analysis in the main chamber where the deposition and irradiation of ice layers is performed. The total gas pressure measured by a Bayer-Alpert gauge was $3.6 \cdot 10^{-11}$ mbar. The intensity scale on this plot corresponds approximately to pressure in mbar units. The most abundant species are H_2 ($m/z = 2$), H_2O ($m/z = 18$), CO/N_2 ($m/z = 28$), CH_3OH ($m/z = 31$) and CO_2 ($m/z = 44$). The level of organic contaminants, toluene or xylene at $m/z = 91$ and 92 , is below 10^{-13} mbar.

So far, we have only performed a few test experiments for calibration, that serve to check the performance of ISAC by comparison to previous results published in the literature. The preliminary data presented below

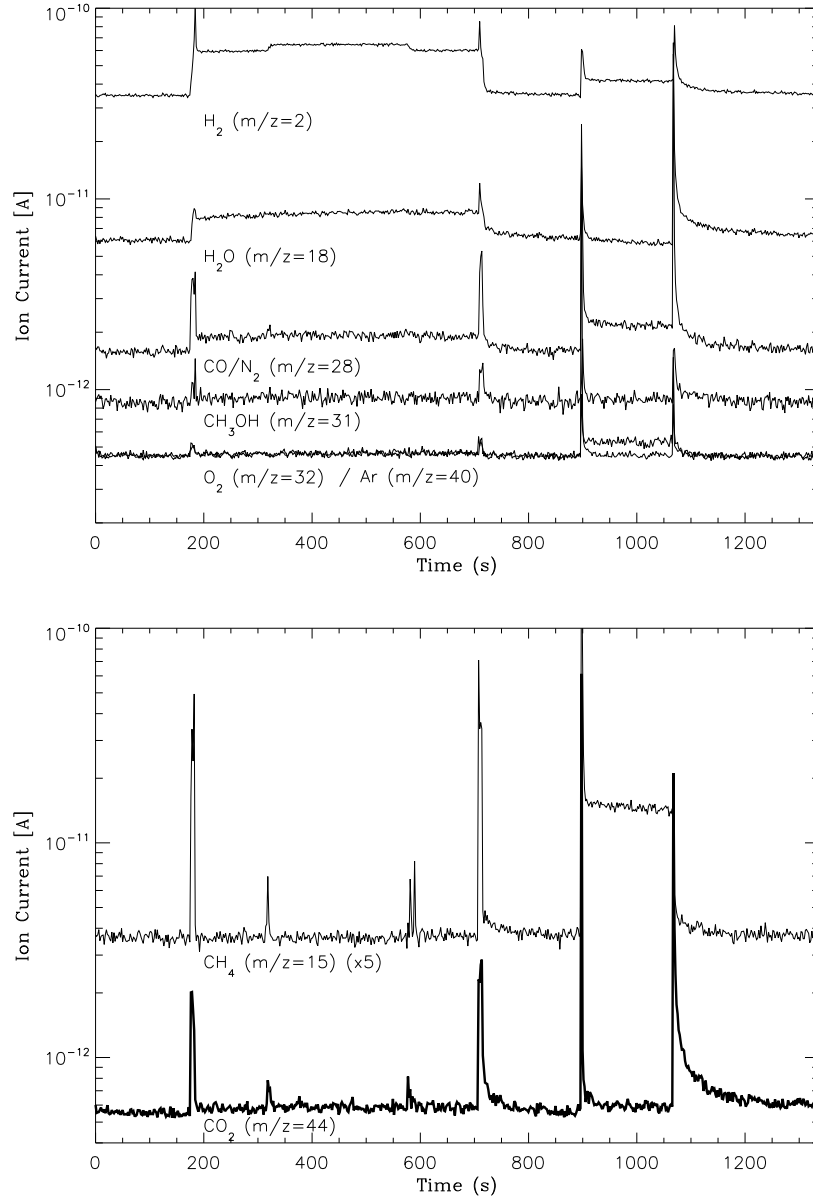


Fig. 4. The evolution of the partial gas pressures is coupled to the operation of the different pumping systems as follows: i) the valve connecting the IGP to the main chamber is closed after 175 s, ii) in addition the TSP valve is closed after 315 s, iii) the TSP valve is opened after 575 s, iv) the IGP valve is opened after 705 s, v) the TMP valve is closed after 895 s, vi) the TMP valve is opened after 1067 s.

corresponds to the deposition and sublimation of CO ice.

The relative concentrations of the gas components in the gas line are monitored continuously, and were found to be very stable even for long duration experiments, i.e. longer than one day. Fig. 5 shows the concentration of gases in the gas line during the deposition. CO, the selected gas for the deposition in this experiment, has a concentration around 99 %, compared to the residual gases that remain in the gas line. Residual H₂O is below 1 % concentration, while the CO₂ and CH₃OH remaining in the gas line from the previous experiment are below 0.1 % concentration.

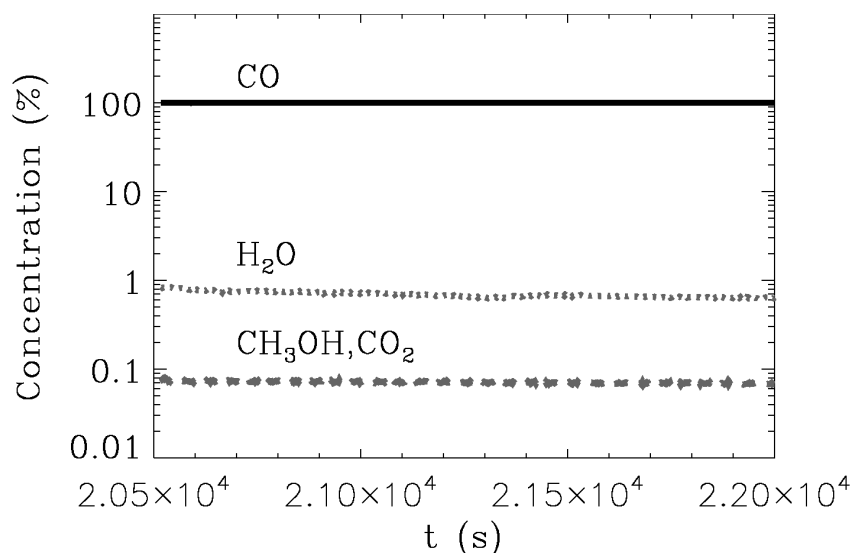


Fig. 5. Relative abundances of CO and the residual gas species present in the gas line during the CO deposition experiment. The y-scale is logarithmic.

The QMS located at the main chamber measures the increase in the partial pressure of CO when deposition is started. This is illustrated in Fig. 6. CO is detected for $m/z = 28$. It is found that $m/z = 2, 18,$ and $44,$ corresponding to H₂, H₂O, and CO₂, also increase during the deposition of CO, but their partial pressures are very low compared to that of the deposited CO.

Once deposition was completed, warmup was started increasing the temperature slowly at 1 K min^{-1} . The QMS detected an increase of CO in the gas phase, reaching a maximum at 28 K, corresponding to the desorption

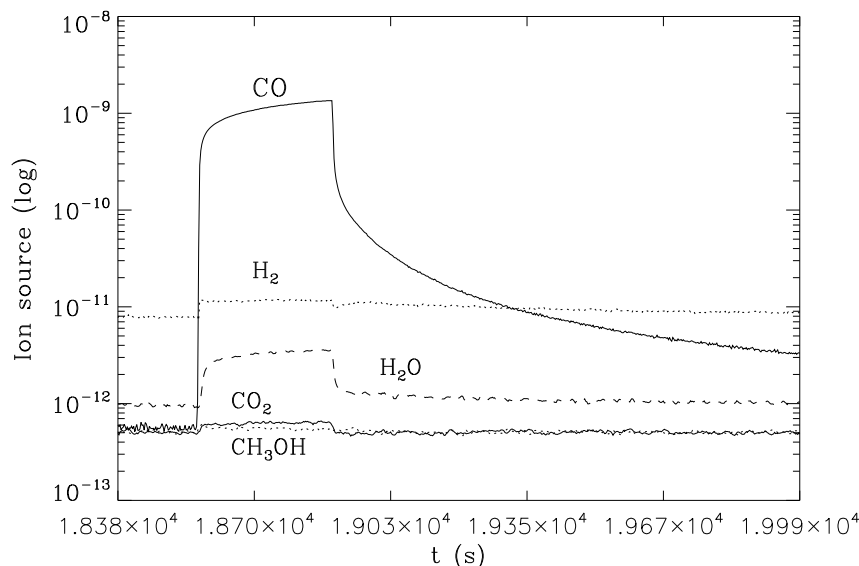


Fig. 6. Partial pressure of CO during deposition. The ion current in A, represented on the y-scale, corresponds roughly to the partial pressure in mbar. The most abundant residual components remaining in the chamber have $m/z = 2, 18, 44,$ and $32,$ and correspond to $H_2, H_2O, CO_2,$ and $CH_3OH/O_2.$

temperature of CO under UHV conditions. This temperature value for the desorption of pure CO ice is in good agreement with the values previously reported.⁸ This is shown in Fig. 7, see figure caption. As CO desorbs a slight increase in the partial pressure of H_2 is also observed. H_2 is not expected to accrete on the substrate at 7 K, the substrate temperature during deposition, but can be trapped in the micropores of CO ice. As an example, the trapping of CO at 10 K in amorphous H_2O ice has been reported.⁹

Fig. 8 presents four infrared spectra corresponding to the stretching mode of CO ice at different temperatures during warmup. Each spectrum corresponds to 128 scans at resolution $2\text{ cm}^{-1}.$

5. Conclusions

The first calibration experiments performed with ISAC indicate that this UHV setup is performing as expected. All components (pumping systems, cryostat, detectors, deposition system,...) are functioning optimally, and the base pressure in the main chamber can be down to $2.5 \cdot 10^{-11}$ mbar. The

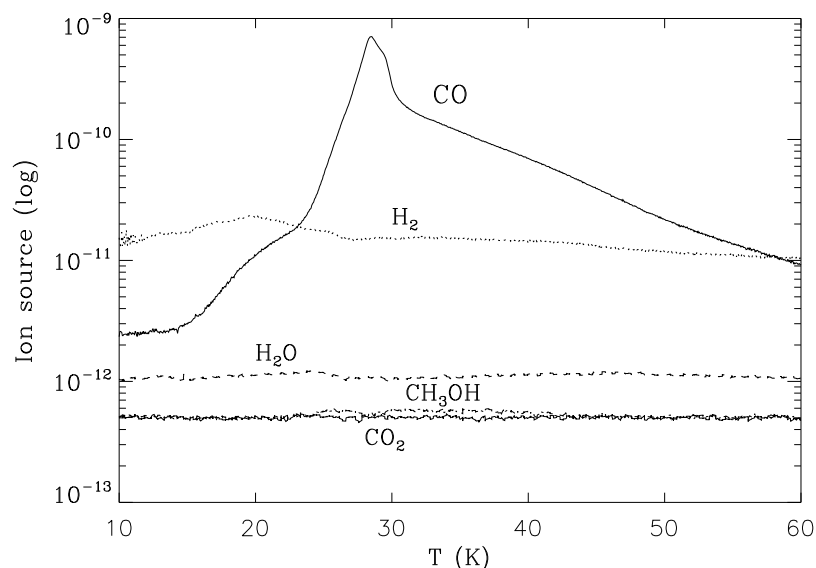


Fig. 7. CO ice desorption during warmup. The main residual gas components are also shown: H_2 , H_2O , $\text{CH}_3\text{OH}/\text{O}_2$, and CO_2 . The current intensity y-scale in A, corresponds roughly to partial pressure in mbar.

QMS was connected to the temperature controller to collect the temperature values during warmup, required to perform temperature programmed desorption (TPD) experiments, see Fig. 7. The system for the preparation of complex gas mixtures, containing H_2O and CH_3OH vapors, and gas components like CO , CO_2 , CH_4 , etc. is probably unique compared to other setups dedicated to astrochemistry. The gas line design that incorporates electrical valves and a QMS monitoring the gas composition, and laminar flow conditions at pressure below 1 mbar, allow the preparation of complex ice mixtures with practically no change in their composition, even for long depositions of the order of one day. This is important for the accuracy and reproducibility of the experiments aiming at the simulation of ice mantle processing in astrophysical environments. The common deposition of gas mixtures under static conditions, typically using a bulb containing a gas mixture with a total pressure of several mbars, does not guarantee the deposition of complex gas mixtures with constant composition, and often the composition of the deposited ice differs from the one expected.

At this stage, ISAC is ready for experimentation aimed to produce rel-

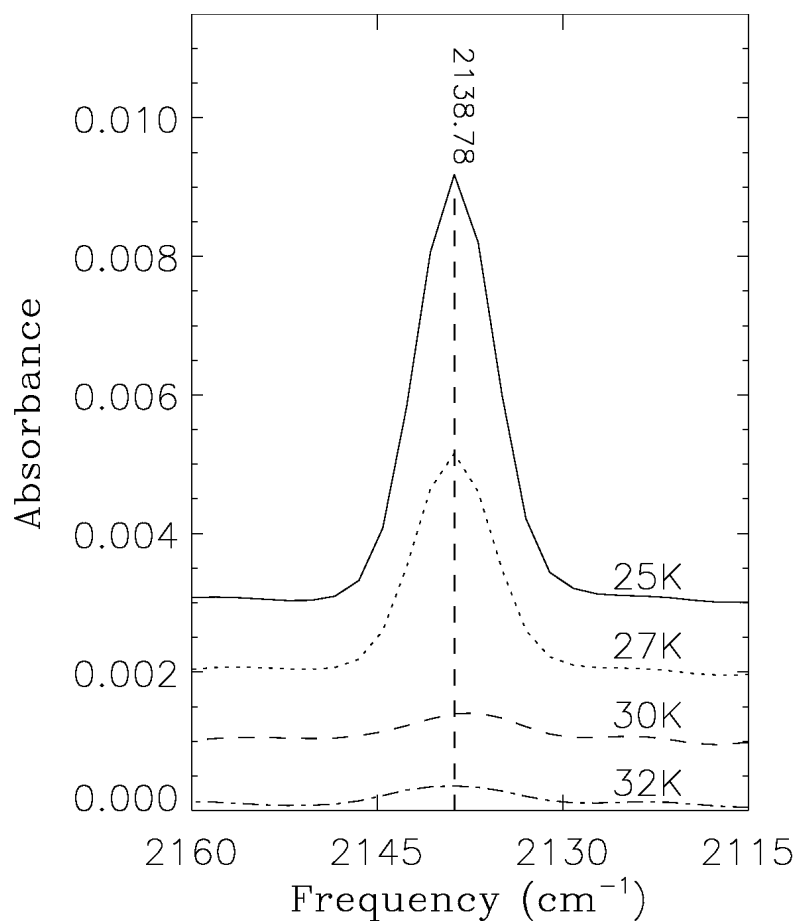


Fig. 8. Infrared spectrum of CO ice at four different temperatures during warmup.

evant scientific results in the fields of laboratory astrophysics and astrochemistry.

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References

1. J. S. Mathis, P. Mezger, & N. Panagia, *A&A* **128**, 212 (1983).
2. C. J. Shen, J. M. Greenberg, W. A. Schutte, & E. F. van Dishoeck, *A&A* **415**, 203 (2004).
3. E. L. Gibb, D. C. B. Whittet, & J. E. Chiar, *ApJ* **558**, 702 (2001).
4. W. F. Thi, K. M. Pontoppidan, E. F. van Dishoeck, E. Dartois, L. d'Hendecourt, *A&A* **394**, L27 (2002).
5. K. M. Pontoppidan, C. P. Dullemond, E. F. van Dishoeck, G. A. Blake, A. C. A. Boogert, N. J. Evans II, J. E. Kessler-Silacci, F. Lahuis, *ApJ* **622**, 463 (2005).
6. G. M. Muñoz Caro, & W. A. Schutte, *A&A* **412**, 121 (2003).
7. P. Jenniskens, G. A. Baratta, A. Kouchi, M. S. de Groot, J. M. Greenberg, G. Strazzulla, G., *A&A* **273**, 583 (1993).
8. K. Acharyya, G. W. Fuchs, H. J. Fraser, E. F. van Dishoeck, & H. Linnartz, *A&A* **466**, 1005 (2007).
9. B. Rowland, M. Fisher, J. P. Devlin, *J. Chem. Phys.* **95**, 1378 (1991).