The hunt for frozen organic molecules in space: a laboratory approach

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Experimental setup and methodology

This chapter presents an overview of the experimental setups used in this thesis and summarizes the used approaches. In the following Sections, an overview of the HV (High vacuum) setup and its upgrade, the IRASIS (InfraRed Absorption Setup for Ice Spectroscopy) setup, as well as the OASIS (Optical Absorption Setup for Ice Spectroscopy) setup is given.

2.1 The HV setup

The HV setup has been used for more than two decades in the LfA, with smaller modifications or experimental upgrades, but performing along the same measuring principle. This setup consists of a stainless steel high vacuum chamber (base pressure $\sim 2 \times 10^{-7}$ mbar) placed in the cavity of a Varian 670 Fourier transform infrared (FTIR) spectrometer. The chamber is pumped by a turbomolecular pump (Oerlikon Leybold TurboVac 361) that is backed by a Edwards E2M8 double-stage rotary vane pump (8 m^3 hr^{-1}). The pressure is measured with an Agilent FRG-720 full-range gauge. In the center of the chamber, there is a ZnSe substrate that is thermally connected to a closed cycle helium cryocooler (Air Products Displex DE-202). The ZnSe can be cooled to temperatures as low as 15 K. The substrate temperature is measured by a silicon diode (DT-670 from Lake Shore Cryotronics) connected to a LakeShore 330 temperature controller. The gaseous sample (pure or mixed) used to grow the ice is stored in a 2L glass bulb attached to the dosing line of the HV setup.

Before the sample deposition, an IR spectrum of the bare substrate is acquired, this is called the "background spectrum". The background spectrum has the purpose of measuring the contribution of the instrument and environment to the spectral signal. These contributions are subtracted from all the sample spectra acquired in the sequence in an automatic procedure performed by the spectrometer. To avoid absorption by atmospheric H_2O and CO_2, present in the optical path of the infrared beam, the system is purged with dry air by a Balston 75-62 FT-IR Purge Gas Generator. The gaseous sample is then admitted into the chamber through a needle valve. The ice is grown by background deposition, which means that the molecules collide with the substrate impacting from random directions. During and after the ice deposition, an FTIR spectrometer (Varian 670) records the spectra in the 5000 – 400 cm^{-1}

(2 – 25 μm) range at resolution from 4 up to 0.1 cm^{-1} (typical values are 0.5 cm^{-1} - 1 cm^{-1}). After the sample deposition, the ice is heated at an adjustable rate (typically 25 K hr^{-1}) until its complete sublimation. During the ice heating, the infrared spectrum of the sample is recorded, which allows for monitoring the change of the infrared profile of the different ice components with temperature. The spectra are acquired by averaging about 128 - 256 scans. The time that it takes to acquire a full spectrum depends on the resolution and the number of scans. Since a spectrum is recorded during the heating of the sample, the scans are acquired at slightly different temperatures. This imposes a temperature resolution for the final spectra that corresponds to a maximum of 3.5 K. In the HV setup, ices are typically grown to a thickness of a few thousand monolayers (column densities of the order 10^{18} molecules cm^{-2}). These thick ices are necessary to ensure that at the relatively high background pressure, the deposition of background contaminants (mainly H_2O and N_2) is negligible.

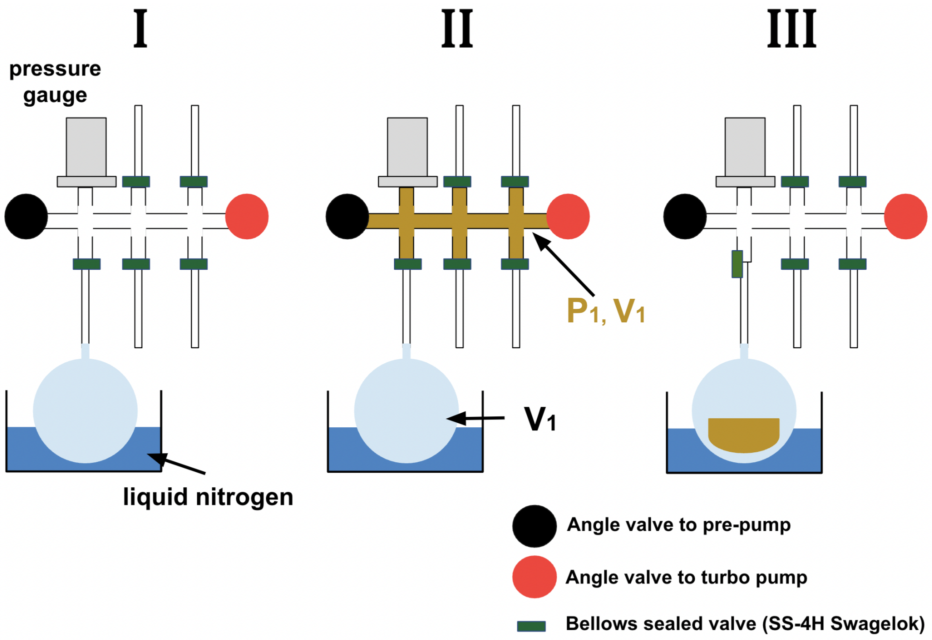

Figure 2.1: Procedure to prepare gaseous mixtures in the mixing system. In I: the bulb and the mixing line used to prepare the mixtures are evacuated to a base pressure of 10^{-4} mbar. The valve to the bulb is closed and the bulb is immersed in a liquid nitrogen container. II: the mixing system is filled with a pressure P_1 of a gas or vapor component. In III: the valve to the bulb is opened and the gas/vapor in the mixing line freezes in the bulb.

The gaseous samples used to grow mixed ices are prepared in a separate mixing system (base pressure $\sim 10^{-4}$ mbar). The pressure in the mixing system is measured using two mass-independent pressure gauges that cover the 0 - 1000 mbar range. All the gaseous samples are prepared in a 2 liter bulb containing a total pressure of 20 mbar. The partial pressure of each component is proportional to their fraction in the mixture. For example, a gas mixture of H_2O:CO_2(2:1) consists of a mixture of $20 \times \frac{2}{3} \sim 13.3$ mbar of H_2O and $20 \times \frac{2}{3} \sim 6.7$ mbar of CO_2. The mixtures are prepared by the sequential freezing of the individual components to the bulb, which is kept immersed in a liquid N_2 container. The procedure for adding individual components to the gaseous mixture is schematically illustrated in Figure 2.1 and described in the following. Initially, the bulb and mixing line are evacuated and the valve to the bulb is closed (shown in I). The mixing line is filled with the desired amount of gas or vapor component (II). The valve connecting the bulb to the mixing line is opened and the content of the mixing line expands to the bulb. If the freeze-out temperature of the gas or vapor component is above the temperature of the liquid nitrogen ($\sim$ 77 K), this component will completely freeze out in the glass bulb, as shown in III. The valve to the bulb is closed, the mixing line is evacuated and the addition of a new component is performed. The partial pressure of the component added to the bulb can be calculated considering the relation $P_1V_1 = P_2V_2$, where P_1 and V_1 are the pressure of the gas when it occupies the volume V_1 (mixing line), V_2 is the volume of the bulb (2 L), and P_2 is the partial pressure of the component in the bulb. In case the freeze-out temperature of the gas component is below 77 K, the gas will expand and occupy the volume of the mixing line and the bulb. In this case, the final volume of the gas will be $V_1 + V_2$ instead of V_2. Gases that freeze out below 77 K are typically added as the last component to the gaseous mixture. Following this methodology, the error estimated for the ratios of a certain component in the gaseous mixtures is estimated as 10%. Additional details about the HV setup can be found in Chapter 2 of the Ph.D. thesis of Terwisscha van Scheltinga 2021.

2.2 IRASIS

In 2020, the HV setup was upgraded to an ultra-high vacuum system, IRASIS, which allows for recording the infrared spectrum of an ice sample and measuring its thickness. In addition, it also allows for measuring the refractive index of ices. Figure 2.2 shows a schematic picture of IRASIS main chamber and its components. The IRASIS setup consists of a stainless steel chamber that reaches a base pressure of $\leq 10^{-9}$ mbar. This lower base pressure decreases the accretion of background gases, which makes this system more suited to grow thinner ices when compared to the HV setup. The center of the vacuum chamber houses a germanium (Ge) window that is connected to a closed-cycle helium cryocooler (DE-202 - Advanced Research Systems) and can reach temperatures as low as 15 K. The cryocooler head is mounted onto a two-stage differentially pumped rotary platform which allows for 360° rotation of the substrate inside the chamber. A Ge substrate was chosen because this material transmits most of the incident infrared light in most of the mid-infrared region and reflects the visible light at 632.8 nm. This allows for recording the infrared spectra of samples in transmission mode and measuring the refractive index using the laser interference technique described in the following sections. The temperature of the ice sample is measured by a silicon diode (DT-670-CU) connected to a Lakeshore 335 temperature controller. The pressure in the chamber is measured with a Pfeiffer PKR 360 C full-range gauge and is also monitored by a Quadrupole Mass Spectrometer (QMS), that was recently added to the system.

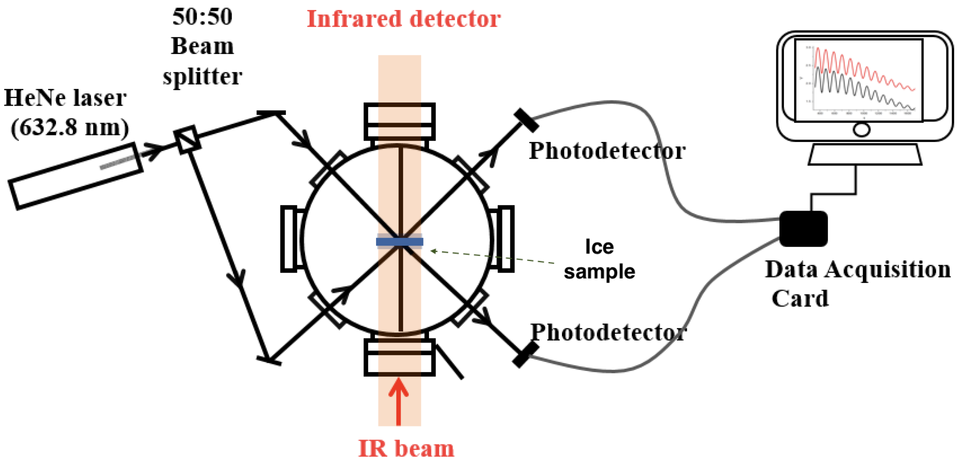

Figure 2.2: Schematic diagram of the IRASIS setup showing a simplified version of the infrared beam path and the laser beams that are used to measure the ice thickness on both sides of the Ge substrate (adapted from Rachid et al., 2021).

IRASIS is coupled to a gas dosing system, which is shown in Figure 2.3 I and schematically depicted in Figure 2.3 II. This dosing system contains three compartments where gases can be stored and independently admitted into the vacuum chamber through adjustable leak valves. Thus, the ice components are mixed during the ice deposition, without requiring the preparation of a gaseous mixtures. This procedure has advantages for controlling the ratios between the different species in the sample, which results in more accurate measurements of apparent band strengths of molecules in ice mixtures (Yarnall and Hudson, 2022). The works presented in Chapters 3, 4 and 5 were done before the implementation and test of this dosing system. Thus, the gaseous samples used to grow the ices were prepared in a glass bulb, following the methodology described in the previous Section. The experimental procedure to calibrate the deposition of individual gases and vapors using the separate dosing lines will be introduced in future works (Slavicinska et al., submitted). The gaseous sample (pure or mixed) contained in a glass bulb is attached to one of the dosing lines of IRASIS and admitted into the chamber through a leak valve. The ice is grown by background deposition on both sides of the Ge substrate. Using a FTIR spectrometer (Varian 670), the mid-infrared spectrum of the sample (2.5 - 20 μm / 4000 - 500 cm^{-1}) is measured after the ice deposition and during the heating. Since the base pressure on IRASIS is more than two orders of magnitude lower than in the HV setup, ices can be made thinner and the contamination from the deposition of background contaminants is negligible.

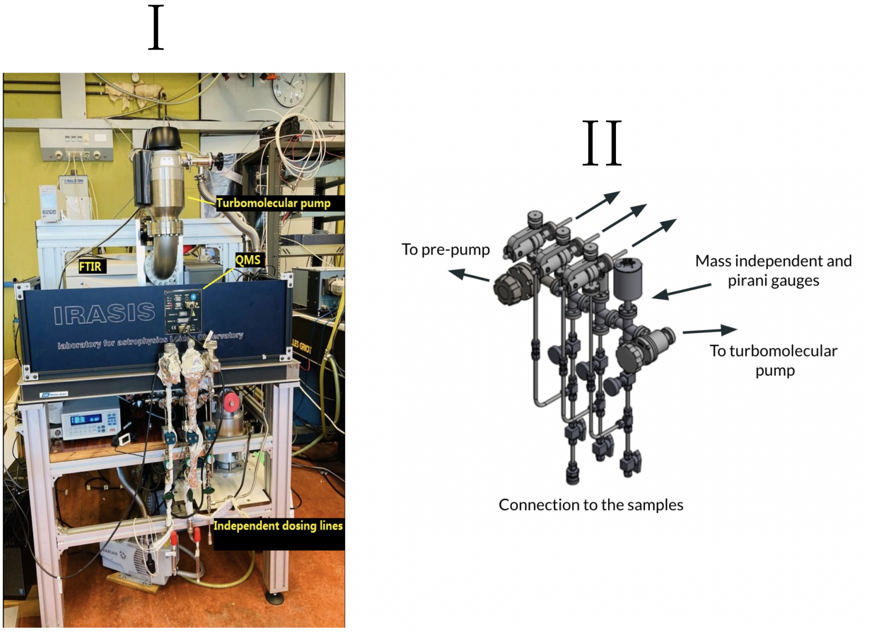

Figure 2.3: Panel I shows the IRASIS setup and panel II shows a schematic picture showing the deposition line.

The number of absorbing molecules in the sample, given by the column density (N, in molecules per cm^{-2}), is related to the area of an absorption feature (i.e., the integrated absorbance of an absorption feature) through a modified version of the Lambert-Beer law:

$$N = \frac{2.3}{A} \int_{\nu} \mathrm{Abs}_{\nu}\, \mathrm{d}\nu, \tag{2.1}$$

where A is the band strength given in cm molecule^{-1}, and the integral of the absorbance is performed over the whole wavenumber region of the absorption feature. The factor 2.3 in the Equation is derived from the conversion of optical depth (τ) to absorbance. The optical depth is related to the transmittance of light by the natural logarithm (τ = -ln(T)), while the absorbance is measured by the spectrometer on the logarithm base 10 scale (Abs = -log(T)).

2.2.1 Thickness and refractive index

In addition to the FTIR spectrometer, IRASIS has a laser system that allows for measuring the ice thickness and refractive index of the ice samples during deposition. For these measurements, a technique based on the interference of light is employed. In this technique, a laser beam hits a growing ice, and the reflected light is recorded and analyzed. When the laser light strikes the ice surface, part of it is reflected in the vacuum-ice interface and part is refracted into the ice. The light rays that are refracted into the ice are eventually reflected by the ice-substrate interface (for reflective substrates). These light rays refract back to the vacuum and interfere with the light rays that are reflected by the ice surface, as illustrated in Figure 2.4. The intensity of the resulting signal depends on the phase difference of the interfering light beams. As the ice grows, the optical path inside the ice increases and the phase difference between the light beams alternate between fully in phase (constructive interference) and out of phase (destructive interference). The result is an oscillating constructive and destructive interference pattern, as shown in Figure 2.4.

The ice thickness (d) can be derived from the interference pattern recorded during its deposition following the relation:

$$d = \frac{m\lambda}{2\sqrt{n^2 - \sin^2\theta}}, \tag{2.2}$$

where λ is the laser wavelength (here 632.8 nm), θ is the incident angle, m is the number of interference fringes, and n is the ice refractive index.

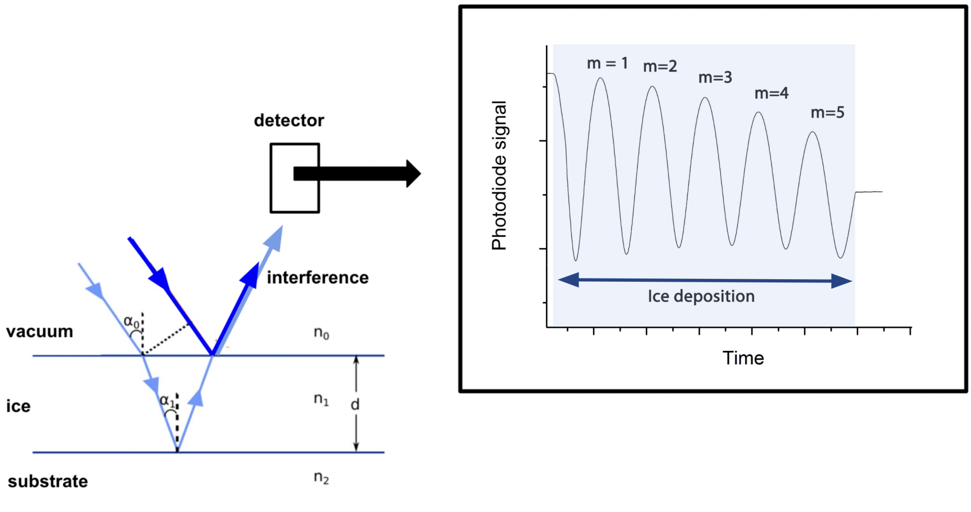

Figure 2.4: Interference of light in the ice sample (based on Chapter 5.

For the refractive index measurements, two laser beams with the same wavelength hitting the ice under different incident angles are employed (see Beltrán et al. 2015). The ice is grown at a constant rate while the interference pattern of both laser beams are recorded, as illustrated in Figure 2.4. The refractive index of the deposited ice is related to the incidence angle and the period of the oscillation patterns by (Tempelmeyer and Mills Jr, 1968):

$$n = \sqrt{\frac{\sin^2\theta_0 - \gamma^2 \sin^2\theta_1}{1-\gamma^2}}, \tag{2.3}$$

where $\gamma = \frac{T_1}{T_0}$ with T_1 and T_0 the period of the interference signals generated by the two laser beams that hit the ice surface at angles θ_1 and θ_0, respectively.

To measure the ice refractive index on IRASIS, the substrate is rotated by 90°. The laser beam is split with a 50:50 cube beam splitter and the resulting beams are pointed to the substrate using a few mirrors. The laser beams hit the ice surface at typical angles of $\sim 5°$ and $\sim 45°$. The produced interference patterns are recorded using individual photodetectors (Thorlabs PDA36A2). During the ice deposition, the pressure in the chamber is kept as constant as possible, since the deposition rate will influence the period of the interference fringes. This is usually performed by filling the dosing line with a pressure of ~ 100 mbar of gas and setting the leak valve at a fixed position. The pressure in the dosing line is high enough to maintain a constant pressure in the chamber during the ice deposition. For depositing vapors from liquids, a glass tube containing the liquid is connected to one of the dosing lines of the system and filled with the vapor. Thus, the pressure in the dosing line is equal to the vapor pressure of the liquid. During the deposition, the glass tube is immersed in a water bath at a constant temperature to diminish variations in the sample temperature (and thus the vapor pressure of the liquid). Before filling the dosing line with vapor, the liquid sample is purified through at least three freeze-thaw cycles. The refractive index of the pure ice sample is calculated using Equation 2.3. The uncertainty in the refractive index of a given ice is calculated through the standard deviation of a collection of measurements performed under similar conditions. In our measurements, this typically amounts to $\leq 5\%$ of the refractive index values.

2.2.2 Apparent band strength measurements

The column density of a molecule in a pure ice can be written as :

$$N = \frac{d\,\rho\,N_{\mathrm{A}}}{M}, \tag{2.4}$$

where d is the ice thickness (in cm), ρ is the ice density (in g cm^{-3}), N_{A} is the Avogadro's number, and M is the molar mass (in g mol^{-1}) of the molecule. Combining equations 2.4 and 2.1 allows for writing the A values of absorption features as:

$$A = \frac{2.3\,M}{\rho\,d\,N_{\mathrm{A}}} \int_{\nu} \mathrm{abs}_{\nu}\, \mathrm{d}\nu. \tag{2.5}$$

Thus, recording the absorption spectrum of an ice sample with a known thickness and density allows for deriving the apparent band strength values of the molecular absorption features. During a typical measurement, the ice thickness and infrared spectrum are monitored during the ice deposition. The growth rate of the integrated absorbance of a band and the ice thickness is measured during ice deposition and used to calculate the apparent band strength using an analogous of Equation 2.5:

$$A = \frac{2.3\,M\,\alpha}{\rho\ \ N_A\,\beta}, \tag{2.6}$$

where α is the growth rate of the integrated absorbance band (band area), and β is the growth rate of the ice thickness, which is calculated during the maxima and minima of the laser interference pattern using equation 2.2. The growth rates of the thickness and integrated absorbance are used in place of the single measurements of thickness and integrated absorbance of the deposited ice. This provides more robust measurements, that are less susceptible to fluctuations when compared to measurements acquired for a single thickness and integrated absorbance values. In Chapters 4 and 5 this method is used to calculate the apparent band strengths of pure CH_3NH2 and CH_3CN ices, respectively.

2.3 OASIS

The measurements presented in Chapter 6 of this thesis are acquired on the OASIS setup (Kofman et al. 2018; Kofman et al. 2019; He et al. 2022). In the last years, the OASIS setup has been mainly employed for measuring the UV-visible spectrum of molecules embedded in ice matrix and the refractive index of pure ices in the 250 - 750 nm range. The refractive index measurements are based on the interference technique described in the previous section. However, instead of using two laser beams, a laser beam and the broadband light of a Xe arc lamp are employed, allowing for measuring the refractive index in the the 250 - 750 nm range (He et al., 2022). In Chapter 6 of this thesis, the interference signal generated during and after the growth of CO ice is analyzed to gain insights into morphology transformations happening in μm-thick CO ice. During the ice deposition, changes in the optical path of the light inside the ice result in an interference pattern. After the ice deposition, changes in the interference signal after the ice growth indicate changes in the optical properties of the ice or the ongoing of structural transformations (e.g., changes in thickness, morphology). The changes in the interference signal after the growing CO ice samples under different experimental conditions (temperature, deposition speed, and ice thickness) are analyzed to understand morphological changes taking place in these ices.

The experimetnal setup consists of a stainless steel vacuum chamber pumped by a turbomolecular pump (Leybold 350 iX turbovac) to pressures of $\sim 5 \times 10^{-8}$ mbar. The pressure in the main chamber is monitored with a Pfeiffer PKR 360 C full-range gauge. An aluminum mirror is located in the center of the chamber and used as a substrate to grow the ice samples. This mirror is thermally connected to a closed-cycle helium cryocooler and can reach temperatures as low as 7.5 K. The temperature is measured by a silicon diode (S950-SM-Cryogenic Control Systems) connected to a Lakeshore 330 temperature controller. During the measurements, a HeNe laser beam (632.8 nm) hits the substrate at angles or around 2° - 4° and is reflected to a photodetector (Thorlabs PDA36A2), where the light signal is detected. The light from the Xe-arc lamp hits the growing ice at angles of 45° and is collected by an Andor 303i Shamrock spectrometer with a 10 μm slit and detected in a thermo-electrically cooled CCD (Andor iDus DV420 OE). The interference pattern originated from the individual light sources are recorded and analyzed. A schematic picture of OASIS is shown in Figure 2.5.

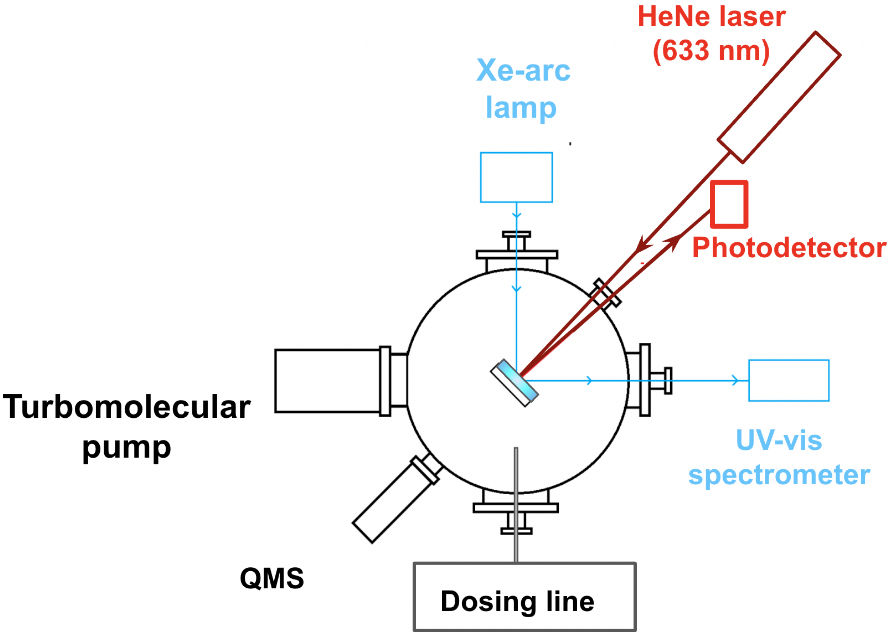

Figure 2.5: Schematic view of the OASIS setup (adapted from He et al. 2022).

The gas used to grow the ice samples is kept in a dosing line and admitted into the chamber through a 1/4” swagelok tube pointed away from the substrate. Thus, the sample is grown by background deposition. The dosing line is typically filled to a pressure of 100 mbar and the gas flow into the chamber is controlled using a leak valve. During the ice deposition, the leak valve is constantly adjusted to maintain a constant gas pressure inside the chamber.

The column density of the ice sample is estimated from the impingement rate of molecules onto the substrate when the chamber is filled to a certain pressure of gas during a certain amount of time, t:

$$N = \frac{\int^{t} P \, \mathrm{d}t'}{\sqrt{2\,\pi\,m\,k\,T}}, \tag{2.7}$$

where P and T are the gas pressure and temperature inside the chamber, respectively,

m is the molecular mass of the deposited molecule, and k is the Boltzmann constant.

2.4 The Leiden Ice Database for Astrochemistry

The spectroscopic data acquired on the HV setup and on IRASIS are publicly available through the Leiden Ice Database for Astrochemistry (LIDA). The interface of the database has functionalities that allow for displaying the infrared spectra of samples at different temperatures and visualize the different vibrational modes of a molecules. The broadband refractive index of pure ices at different temperatures recorded on OASIS are also available from LIDA. In addition to the laboratory data, LIDA also has two online astronomy oriented tools. The SPECFY tool allows to create synthetic spectra of ices observed toward protostars by using template spectra of young stars, from the literature and available through the database, and the laboratory data of ice analogs. The second tool is a complex refractive index calculator, that uses the laboratory infrared spectrum of interstellar ice analogs to calculate the mid-infrared refractive index of the sample. An overview of the current data available from the database, its functionalities, online tools, and examples on how to use them for support interstellar ice research is presented in Rocha et al. (2022).

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