A simulation chamber for absorption spectroscopy in planetary atmospheres.

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Abstract.

A novel simulation chamber PASSxS (Planetary Atmosphere Simulation System for Spectroscopy) has been developed for absorption measurements performed with a Fourier Transform Spectrometer (FTS) and, possibly, a cavity ring down (CRD) spectrometer, with a sample temperature ranging from 100 K up to 550 K, while the pressure of the gas can be varied from

5   10 mbar up to 60 bar. These temperature and pressure ranges cover a significant part of the planetary atmospheres in the solar system and the absorption chamber can thus be used to simulate planetary atmospheres of solar planets and extra solar planets with similar atmospheres. The optical absorption path for the FTS absorption measurements is 3.2 m, due to the implementation of a multipass setup inside the chamber. The FTS measurements cover a wide spectral range, from the visible to the mid-infrared with a sensitivity sufficient for medium strength absorption bands. The FTS has been used previously to measure high pressure

10   atmospheres, including collision induced absorption bands and continuum absorption at ambient temperatures. PASSxS allows to measure the temperature dependence of collision induced bands and continuum absorption, which is important both for the modelling of planetary atmospheres as well as for fundamental processes involving collisions between molecules and atoms.

1   Introduction

The study of planetary atmospheres is important for exploring atmospheric composition and chemical and dynamical processes

15   in solar and extra solar planets, and might provide also valid information on the possibility of existence of forms of life. Many space missions targeting planets of the solar system have been equipped with optical sensors in various spectral ranges with the goal to measure the composition and the radiative properties of the atmosphere. These can provide information about geological processes, such as vulcanic and tectonic activities, temperature profiles, the presence of liquid water, necessary for the existence of life, and the formation of clouds. Most of the sensors used on orbiting platforms are passive sensors,

20   integrating the emitted radiation from the surface or from the lower atmosphere up to the space craft in orbit. Careful analysis of these observations, along with a good knowledge of spectral information, line-broadening processes as well as atmospheric chemistry of all chemical compounds present in different layers of the atmosphere (atoms, molecules, clusters, radicals, ions) may provide profiles of the concentrations of all absorbing, and sometimes non-assorbing, chemical species. Much of the

required knowledge is available from laboratory experiments as well as satellite observations of the Earth, supported by a
well developed theory of absorption and emission processes. Unfortunately the laboratory absorption measurements at high
pressures for a large temperature range are far from complete. This puts a severe limit to the exploitation of high pressure
planetary atmospheres at extreme cold or hot conditions with respect to Earth. Previously we have performed FTS meaurements
at high pressure (up to 40 bar) and high temperature (up to about 500 K) (Stefani et al., 2013, 2018) by using a commercial
absorption cell characterized by a short optical path (about 2 cm). Here we propose a newly designed absorption chamber which
can be cooled down to 100 K and heated up to 550 K, with a long effective absorption pathlength, in contiguous measurement
sessions, without changing the gas sample.

The main requirements for this absorption chamber can be summarized as follows.

1. The optical materials as well as vacuum sealings for optical windows have to be compatible with cryogenic temperatures
   as well as temperatures up to 550 K, and should support pressures up to at least 60 bar.

2. An efficient and well-distributed heating and cooling system is necessary to obtain a uniform temperature of the sample
   gas.

3. Safety measures are required to deal with accidental events during the operation of the system.

4. A stable optical interface with the FTS (and in the future with a CRD) is needed, as well as the maintenance of a stable
   alignment during heating and cooling.

Here we present a facility for performing absorption measurements in gases or mixtures of gases at intermediate pressures
(up to 60 bar) at temperatures ranging from 100 to 550 K. Although several facilities are mentioned in literature for optical
measurements in gases, up to our knowledge, none of these obtain the combination of pressures and temperatures obtained
with PASSxS.

2 Heatable and coolable absorption cells in literature

Several heatable absorption cells have been developed in the past, with the goal to perform spectroscopic studies of hot gases.
More than fifty years ago Abu-Romia and Tien (1966) reported a high temperature absorption cell, using a 20 cm cell with
sapphire windows heated in a furnace capable to reach temperatures of 1200 K and pressures up to 4 atm. Hartmann and Perrin
(1989) used a 11.4 cm long heated cell to measure the absorption of 1% CH_4 in N_2 at a wavelength of 3.384 μm at pressures
between 0.5 and 1.5 atm in a temperature range of 290-800 K. Hartmann et al. (1993) studied the continuum absorption of water
vapor for temperatures and pressures in the 500-900 K and 0-70 atm ranges, respectively, in the 1900-2600 and 3900-4600
cm^{-1} spectral ranges.

Rieker et al. (2007) measured near-infrared anbsorption spectra of water vapor, by using tunable diode lasers and a heatable
Inconel cell with a pathlength of 37.6 cm, equipped with tapered sapphire windows and copper seals. Schwarm et al. (2019)
constructed an absorption cell for spectroscopic measurements in the mid-infrared range, capable to withstand pressures up to

55 200 atm and temperatures up to 1200 K. Such high temperatures are of particular interest in combustion processes. They used CaF$_2$ or sapphire rods with a length of 15 cm, sealed with a high-temperature epoxy to cooled end caps, while only the central part of the absorption cell was heated in a furnace. They reported a temperature uniformity of $\pm$ 7 K at 542 K in the 9 cm long absorption cell . A similar cell has been reported by Almodovar et al. (2019) with a longer pathlength (21 cm) and a slightly worse, but still very good temperature uniformity ($\pm$ 19 K at 802 K). Also Christiansen et al. (2016) used a short pathlength

60 cell (3 cm) equipped with sapphire windows inserted in a furnace to measure CO and CO$_2$ at high pressures and temperatures. They reported a temperature uniformity of $\pm$ 1 K at 1000 K.

The short pathlength cell (2 cm) (AABSPEC, model 2T-AWT) used by Stefani et al. (2013) supports pressures up to 200 bar. This cell uses a double chamber design; the windows of the sample chamber can be heated up to 650 K, but are not subjected to a pressure difference. The outer chamber is filled with a non-absorbing buffer gas and kept at ambient temperature with a

65 closed circuit water cooling. The external windows are thus subject to a pressure difference, but are at ambient temperature. Kalrez O-rings were used to seal the hot windows.

All the cells mentioned before are heatable cells. Coolable cells have been used for many decades, with pioneering work by McKellar and co-workers (McKellar et al., 1970). Typically these cells where coupled to a Fourier Transform Spectrometer and used to measure spectra of molecular complexes (clusters). Ballard et al. (1994) reported such a cell with the possibility

70 to study gases at pressures up to 5 bar. Several coolable cells with multiple reflection optics have been reported with very long pathlengths (see e.g. Horn and Pimentel (1971) (2540 m), Kim et al. (1978) (1500 m) and Briesmeister et al. (1978) (500 m)). A review of coolable cells can be found in Le Doucen et al. (1985).

Very few absorption cells have been constructed with the possibility of heating and cooling; one example can be found in (Schermaul et al., 1996).The cell developed by Schermaul et al. (1996) consists of a 3 m Pyrex glass tube embedded in a

75 quartz-sand bath which can be heated by resistive heating elements and cooled by circulating a coollant. The cell temperatures vary from 123 to 423 K, at atmospheric pressures. The windows are kept at room temperature. Shetter et al. (1987) constructed a long path cell for absorption measurements at temperatures from 215 to 470 K at pressures up to 10 atm. They designed a cell consisting of three concentric stainless steel tubes, the innermost housing White-type optics. They flowed a cooling/heating fluid between the two inner tubes and used the outer tube to create a vacuum to provide thermal insulation. The maximum

80 optical pathlength obtained was 96 m. Table 1 shows a non exhaustive list of heatable and coolable absorption cells reported in literature, for spectroscopic measurements of pure gases and mixtures, with some relevant parameters and is meant to show the state of the art in this field.

PASSxS has been designed as a large volume, long pathlength absorption cell with the possibility to cool and heat the cell while at pressures up to 60 bar. While most previous heatable absorption cells are short pathlength cells (less than 0.5 m) the

85 maximum pathlength of the White cell optics inside PASSxS is 9.6 m. Moreover, PASSxS can also be cooled to 100 K, without changing optics or seals. The chamber allows to vary the temperature from 100 K to 550 K while keeping the same gaseous sample. By performing these temperature scans for different pressures (densities), the temperature dependence of spectral features due to pressure broadening, such as line broadening, collision induced bands and the so-called continuum absorption

can thus be determined. It is well known that these processes are proportional to the square of the density, but their temperature

90   dependence is still under study, both from an experimental and theoretical point of view.

3   General aspects of the simulation chamber

The simulation facility consists of two concentric chambers (see Figure 1), the inner one containing the gas or mixture of gases and the external one ensuring the thermal insulation from the laboratory environment. To this purpose, a medium vacuum (10^{-3}- 10^{-2} mbar) is maintained between the two chambers by means of a rotary pump. Moreover the sample chamber is

95   mounted on three thermally insulating supports, made principally of MACOR rods (see Figure 1), while all connections for cooling, heating and the gas supply to the sample chamber have been also thermally insulated from the outer chamber by using double wall stainless steel tubing. The volume of the sample chamber is about 11 l, while the outer chamber has a volume of about 62 l and may thus function as a buffer in case of a gas leak from the sample chamber.

    The outer vessel is supplied with several vacuum ports for pumping, electrical connections, gas input and output and liquid

100   nitrogen input and output, as can be seen in Figures 1 and 2. The pressure of the gas is measured with a pressure gauge (JUMO MIDAS Type 401001) with a range from 0 to 60 bar. This gauge has a zero offset of less than 0.3% full scale and less than 0.5 % full scale linearity error.
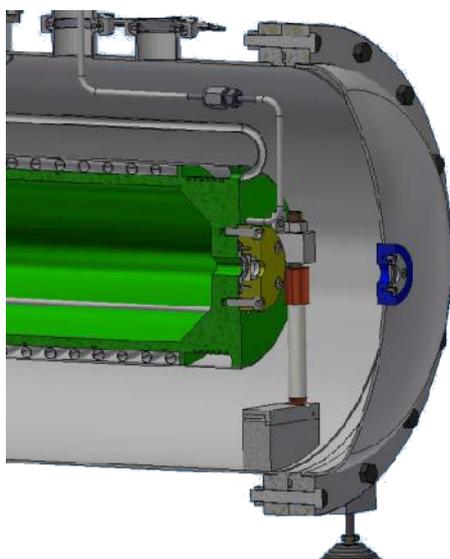
Figure 1. Section of the atmospheric simulation chamber.The sample chamber is indicated in green, while the external chamber is indicated in gray. One of the three insulated supports of the sample chamber can also be observed as well as the cooling circuit.

The sub-systems of the simulation facility have been schematically depicted in Figure 2). The four sub systems are :

1. A cooling system (indicated in blue).

2. A heating system (indicated in red).

3. A set of 6 type T thermocouples to measure the temperature (indicated in green).

4. A gas inlet and outlet system (indicated in violet).

The cooling is achieved with a flow of liquid nitrogen regulated by a dedicated PID controller. The liquid nitrogen flows through stainless steel tubings in close contact with the inner cylinder and through double wall stainless steel tubing on the flanges, as shown in Figure 1. The tubings have been dimensioned to obtain a heat exchange proportional to the masses to be cooled. The total volume of the cooling circuit is 4.3 l and the flow of nitrogen is 5-10 g/s. The cooling circuit consists of two parts, one is cooling the removable flange, which provides optical access, the other circuit cools the body of the cell, with the counter flange and the welded flange. Temperature regulation is achieved by controlling the flow of liquid and gaseous nitrogen in the cooling circuit.

The heating is done by four tubular resistors with a total heating power of 2600 W. Two resistors of 400 W are used to heat the counter flange (heater 2, see figure 2) and the bottom flange (heater 4), both welded to the cylinder and two resistors of 900 W are used to heat the cylinder (heater 3) and the removable flange (heater 1). The temperature is measured on six different places, four type T thermocouples have been mounted on several parts of the cell and two inside the cell, measuring the temperature of the gas in two different positions. The gas outlet is supplied with a safety valve, to avoid that the pressure in the sample chamber exceeds a preset value (70 bar).
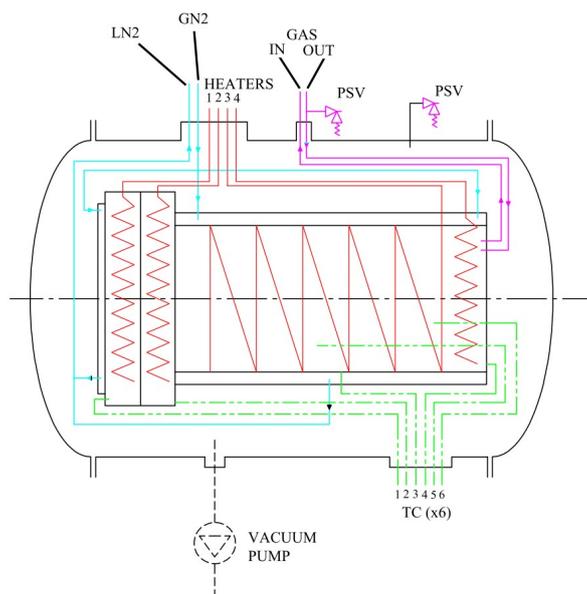
Figure 2. Schematic view of the sub-systems. The heaters are indicated in red, the liquid nitrogen circuit in blue, the thermocouples in green and gas supply lines in violet.

4 Optical Windows and Vacuum Sealings

As shown in Figure 3, the simulation chamber is equipped with two optical windows for the entrance and exit of the light beam from the FTIR spectrometer and other two windows for the entrance and exit of the laser beam for future cavity ring down experiments.
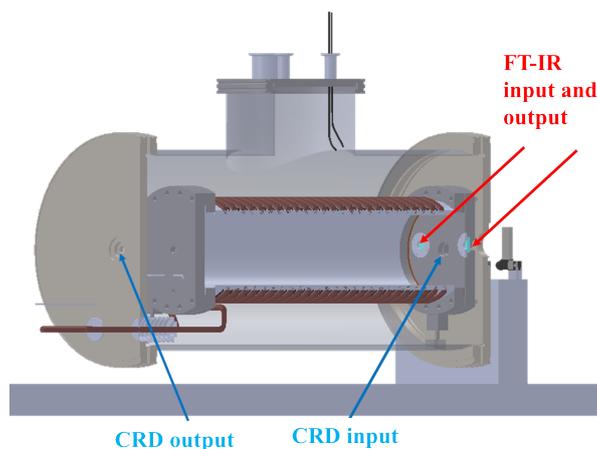
Figure 3. Position of the windows dedicated to FT-IR spectroscopy (red arrows) and to CRD experiment (blue arrows)

125   These optical windows have to satisfy several requirements. First of all their thermal properties have to be compatible with the temperatures of the absorption chamber (100 to 550 K) and they have to be resistant to thermal shock. Secondly, their mechanical properties have to guarantee that they are stable under high pressure. The usual seals for optical windows, such as neoprene, Viton, Teflon and others are not suitable for the full temperature range of the simulation chamber, and thus a different solution had to be found. Metal C-ring seals are suitable for low and high temperatures and can be used in a pressure

130   range from vacuum to more than 5000 bars. They also need a low to moderate sealing load which implies that they can be used with rather soft flange materials. This does not include all optical materials however; when we tried to use ZnSe windows, we observed that the C-rings caused an indent in the material after heating. Based on the hardness of the different optical materials (see Table 2), also BaF_2, CaF_2 and NaCl are probably too soft to be used with C-rings. On the other hand sufficiently hard materials, such as sapphire, Si, fused silica, fused quartz, BK7 glass and borosilicate glass are compatible with metal C-rings.

135   The minimum thickness of an optical window can be calculated by using the formula

$$t_{min} = K \times R \sqrt{\frac{P \times F}{M_R}} \tag{1}$$

where t_{min} is the minimum thickness, K is the fraction of the window subject to a pressure difference, P is the pressure difference, R is the radius of the window, F is the safety factor and M_R is the modulus of rupture. The commonly used safety factor used for pressure vessels is between 3.5 and 4. The minimum thickness for windows of different optical materials has

140 been calculated for a safety factor of 4, K =0.8, a pressure difference of 60 bars and a radius of 12.5 mm and displayed in Table 2. Since the simulation chamber should support many thermal cycles, it is preferable to use materials with a good resistance to thermal shocks, which relates to a low thermal expansion coefficient and a good thermal conductivity. All materials in Table 2, except for BaF_2, CaF_2 and NaCl fulfill this requirement. Then of course the optical properties are important, in terms of spectral transmission and overall transmission. The materials with a high index of refraction (Si, ZnSe and ZnS)

145 have a reduced transmission, which may have an important impact on the optical signal at the exit of PASSxS, considering that all optical experiments need two window transits. This problem might be mitigated by using optical coatings, but one must verify that the coatings are stable at high temperatures. For what concerns certification of optical windows for high pressures and temperatures, certified sight windows are available in fused silica, fused quartz, sapphire and borosilicate (see e.g. https://rayoteksightwindows.com/). Presently the simulation chamber is equipped with 3 mm thick sapphire windows.

150 Also the outer chamber has to be equipped with two sets of windows, but since these are at ambient temperature and support a pressure difference of 1 bar, vacuum sealings and window properties do not pose severe requirements. Presently PASSxS has been equipped with windows in CaF_2 and fused silica for the outer chamber.

5 Safety

Operating the simulation chamber in a laboratory requires that several safety measures are in place. The main risk is the rupture

155 of one of the optical windows in the high pressure chamber. A safety valve can be used to avoid that the pressure in the inner chamber exceeds the maximum operating pressure. The cell will not be operated at pressures exceeding 60 bars, although the design maximum pressure is 100 bars. But a rupture of a window might occur and this would cause a flow of the gas in the outer chamber and a rupture of the windows of the outer chamber, with a consequent emission of the gas in the laboratory. A rupture disc, also known as a pressure safety disk can avoid the rupture of the windows in the outer chamber and can be

160 combined with controlled expansion of the escaping gas. One should bear in mind that the volume of the outer chamber is about 5-6 times (62 L vs 11 L) larger than the inner chamber, and thus the maximum pressure in the outer chamber will be reduced due to the expansion in the larger volume and can be easily handled after the rupture disc. Furthermore, a safety valve will open if the maximum pressure at the gas inlet will be exceeded: In case of failure of the temperature control, or if a too high temperature will be reached, a redundant temperature measurement has been put in place to shut down the heating when

165 the temperature reaches a preset threshold.

6 Optical Interfaces and alignment

Figure 4 shows the transfer optics for the FTIR spectrometer. The collimated parallel beam of the FTIR spectrometer is focused with an off-axis parabolic mirror (focal length 30 cm) and deflected by a plain mirror to produce a focal point at the entrance of the multipass White cell optics (CIC Photonics) inside the pressure chamber and a spot with a maximum diameter of 25 mm

170 on the two focusing mirrors of the White cell. A similar combination of a flat folding mirror and an off-axis parabolic mirror is
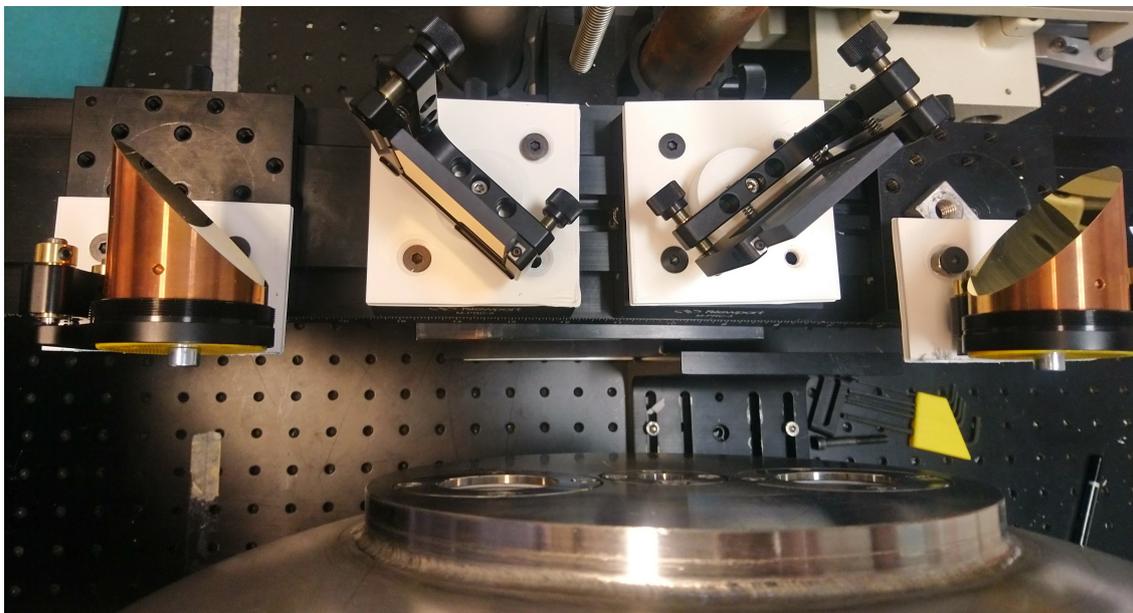
Figure 4. The transfer optics for the FTIR is shown.

producing a collimated exit beam, that is successively focused with short focal length off-axis parabolic mirror on a detector. The White cell optics inside the pressure chamber has a base length of 20 cm, and has been aligned to obtain a pathlength of 3.2 m. An effective optical path length of 9.6 m is feasible, but presently we choose for a more conservative alignment, to facilitate the coupling with the FTS. The mirrors of the White cell are fabricated out of stainless steel and have a protected gold-coated

175   mirrors with proprietary strata that bonds the reflective coatings and protects the mirrors from chemical attack. These mirrors provide over 98.5% reflectivity in the mid-infrared region, thus providing an extraordinary optical power throughput. The FTIR spectrometer, the transfer optics and the simulation chamber have all been mounted on the same anti-vibration optical table and provide a stable alignment. The inner chamber has been mounted on three ceramic (MACOR) supports, one of these can be seen in Figure 1, fixed at the height of the optical plane of the multipass optics. We estimate that the central plane of the

180   sample chamber will be stable within $\pm$ 0.2 mm with respect to the position at room temperature, during the heating and cooling processes. The base length of the White cell optics will vary less than $\pm$ 1 mm during heating and cooling. These small displacements, due to the thermal expansion or contraction, will not affect the alignment of the FTS beam significantly. The optical configuration of the White cell fixed inside the sample chamber is shown in Figure 5.
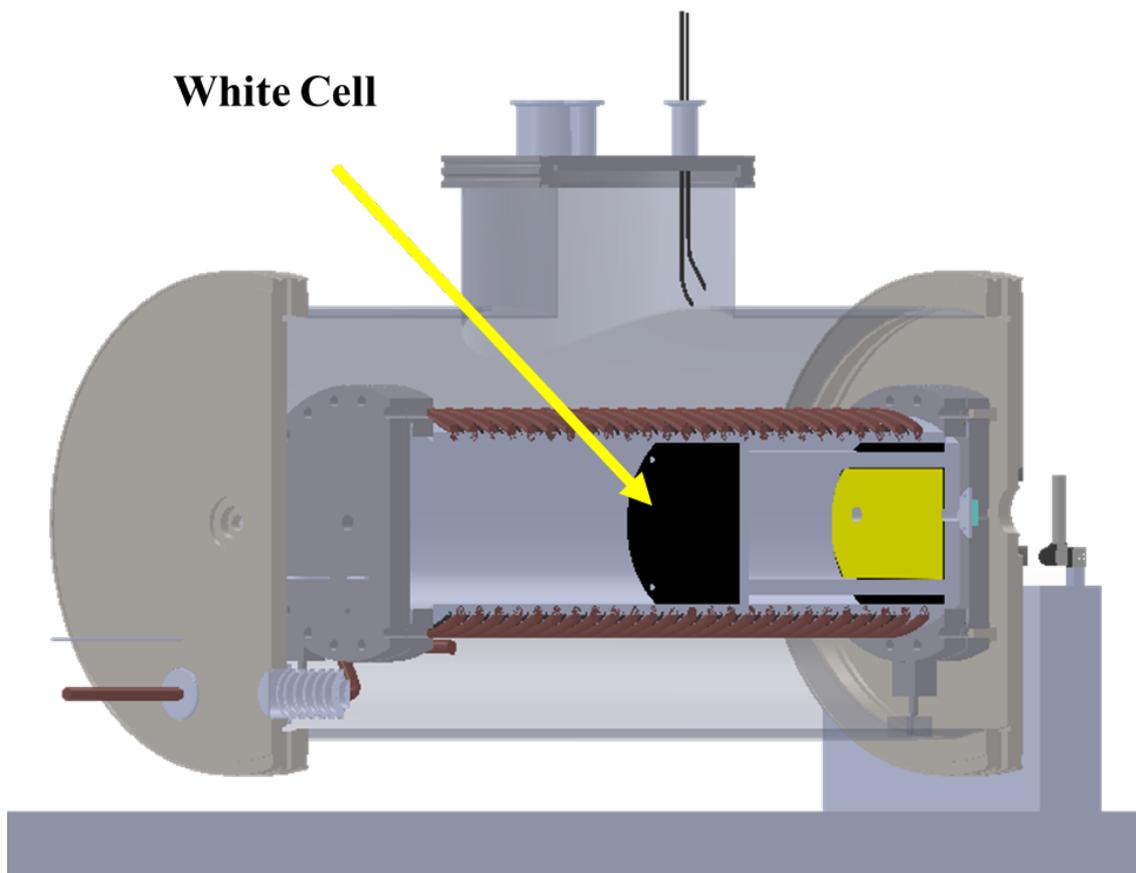
Figure 5. The configuration of the White cell installed inside the sample chamber

7 Tests of the PASSxS

7.1 Heating and cooling tests

The heating is performed by using four tubular resistors, three of them used to heat the flanges and the fourth to heat the body, as shown in Figure 2. The cooling is achieved with a flow of liquid nitrogen which is divided in separate circuits of tubings which have been dimensioned to obtain a heat exchange proportional to the masses to be cooled. A dedicated PID controller has been developed using a software in Labview to stabilize the temperature of the sample chamber. Figure 6 shows a typical cooling and heating test.

The chamber, filled with about 3.75 bar of argon at room temperature, has been cooled with a liquid nitrogen flow up to a temperature of 90 K. The maximum cooling rate is about 32 K/ h. At 90 K the liquid nitrogen flow has been stopped, leading to a gradual warming of the sample chamber with a rate of about 3.3 K/h. At about 140 K we observe an onset of heating, but
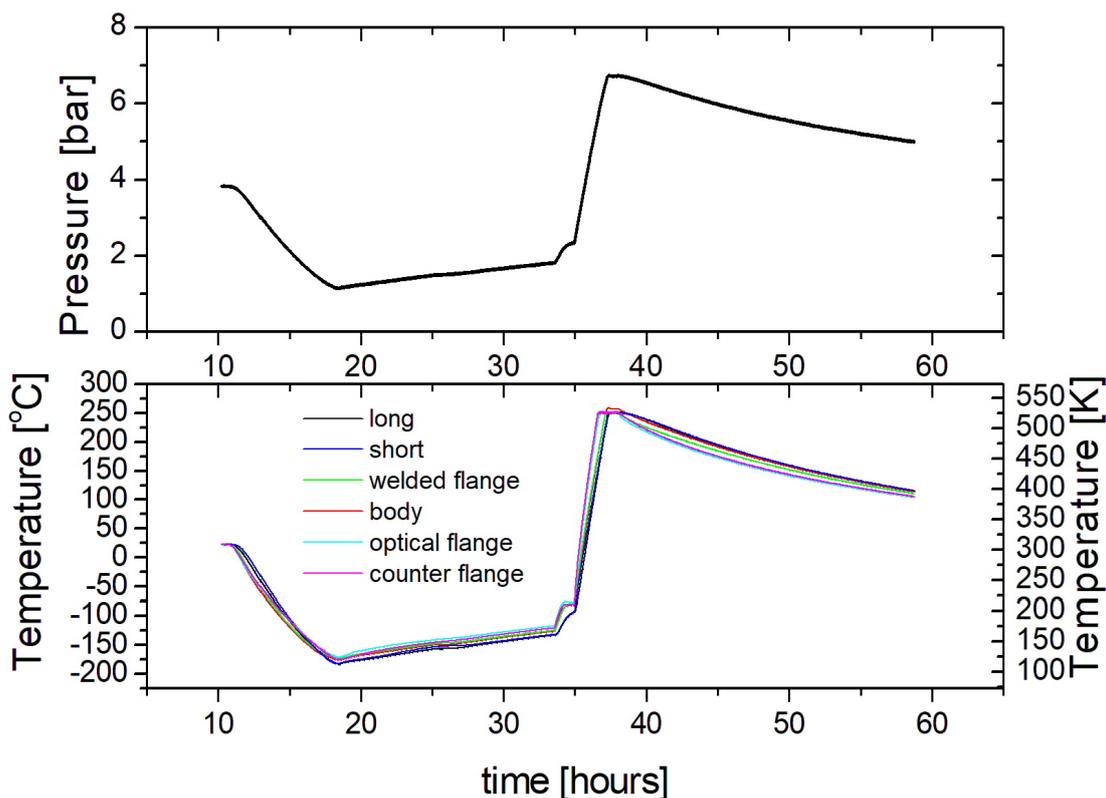
Figure 6. Cooling and heating test of PASS*x*S with about 3.7 bar of argon in the sample chamber at room temperature. Upper panel: The pressure of the Ar is indicated in bars. Lower panel: The light blue and red curves refer to the temperatures recorded by the short and long thermocouples put inside the inner cell (6 and 5 in Figure 2). The blue, green, violet and purple curves refer to the temperatures acquired by the other thermocouples (4,3,2,1 in Figure 2) respectively.

no linear behaviour. This might be due to residual nitrogen gas in the circuit. From 180 K a linear heating is observed, caused

195   by switching on the four heaters at full power. The sample chamber is then actively heated with the four heaters indicated in Figure 2 from 180 to 540 K, with an average heating rate of 144 K/h. The heaters have been switched off at 540 K and the chamber cooled down with a cooling rate of about 6.2 K/h. This shows that heating is much more efficient than cooling and that in absence of cooling and heating the temperature of the sample is relatively stable and reaches an equilibrium with the ambient temperature with a rate of 3-6 K/h. This slow equilibration is due to the large heat capacity of the sample cell and the

200   good thermal insulation.

   The temperature of various parts of PASS*x*S has been measured with 6 thermocouples. Two thermocouples are suspended in the gas, at different distances from the welded flange and are called long and short. The other four thermocouples have been

mounted on 4 parts of the absorption cell; welded flange, optical flange, the cylindrical body of the cell and the counter flange. Each of these parts is heated by a separate heater.

205   If we assume that the gas in the sample cell is in thermal equilibrium, the pressure of the gas can be used to calculate the temperature of the gas. We assumed that the temperature as measured at the start of the test should correspond with the calculated temperature. This yielded a density of 0.1562 mol/l, which allowed us to calculate the gas temperature for the rest of the experiment, by using the NIST database for fluids and gases (https://webbook.nist.gov/chemistry/fluid/) and to compare this with the temperatures measured by the thermocouples in the gas. In general there is a good agreement (better than $\pm$ 2 K)

210 between the calculated temperature and that measured with the thermocouple in the center of the cell (referred to as "long") if the cooling and heating is slow enough for allowing the gas to reach an equilibrium with the cell (see Figure 7) . If the heating or cooling is too fast, the measured temperatures (long and short) may lag behind with respect to the temperature calculated from the pressure. Probably the calculated temperature is more representative for the gas temperature than the measured one.
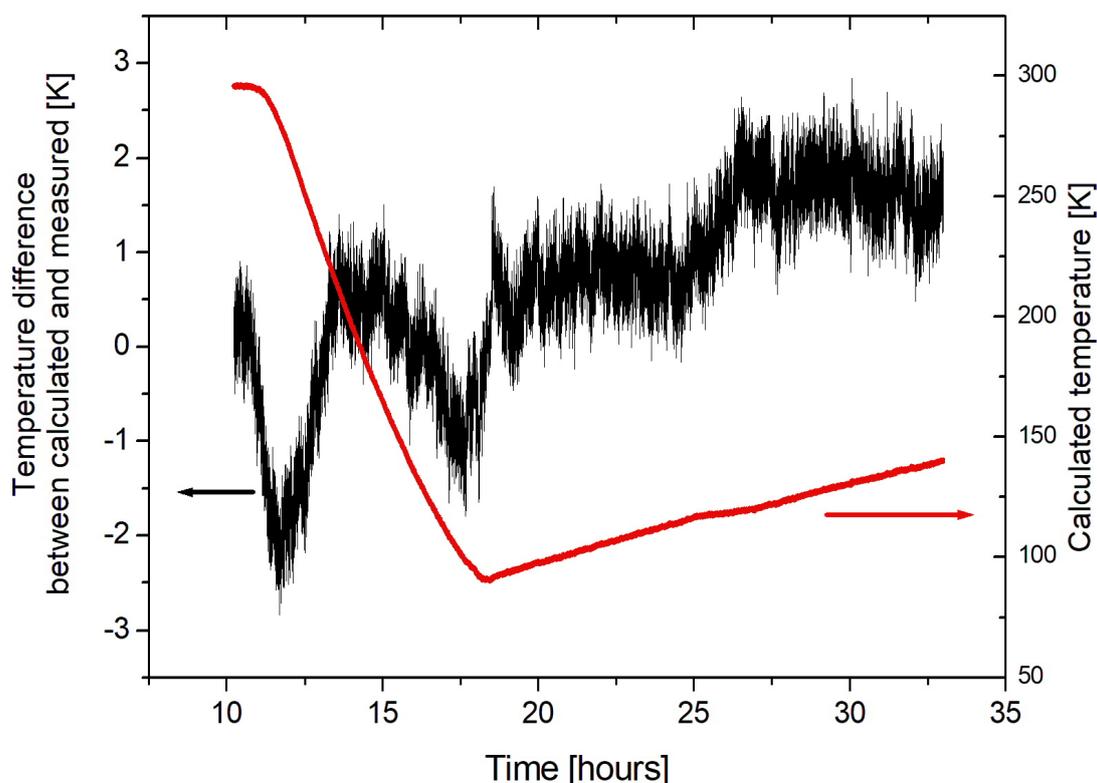
Figure 7. The difference of the temperature calculated from the pressure of the Ar gas with respect to the gas temperature measured by the "long" thermocouple has been displayed (black curve). The agreement is $\pm$ 2 K. The red curve corresponds with the calculated gas temperature.

FTIR measurements at relatively low spectral resolution (1-2 cm^{-1} FWHM) require only a few minutes to record 100-200
215 scans, sufficient for a good signal-to-noise ratio. The temperature of the gas during such a measurement can be considered
constant up to a good approximation. The drawback of such a passive thermal stability is that it would take between 40 and
50 hours for the sample to return to ambient temperature, starting from the maximum or minimum temperature. Another
approach would be to cool the sample down to 90 K and then heating the cell with moderate power to reach 500 K in 4-5 hours.
It is important to verify if the different parts of the sample chamber are in thermal equilibrium during passive cooling and
220 heating. We observed that during the cooling process and the successive passive heating the temperature differences between
the different parts of the cell as measured by the four thermocouples, were small (typically less than 10 degrees).

However, we observed that when we supplied the maximum power to all four heaters, some parts of the cell (the optical
flange and its counter flange) were much hotter than the body and the welded flange, so we regulated the power to each heater
in a way that all parts would have similar temperatures at all times. This resulted in much smaller temperature differences
225 during the active heating process (typically less than 10 degrees).
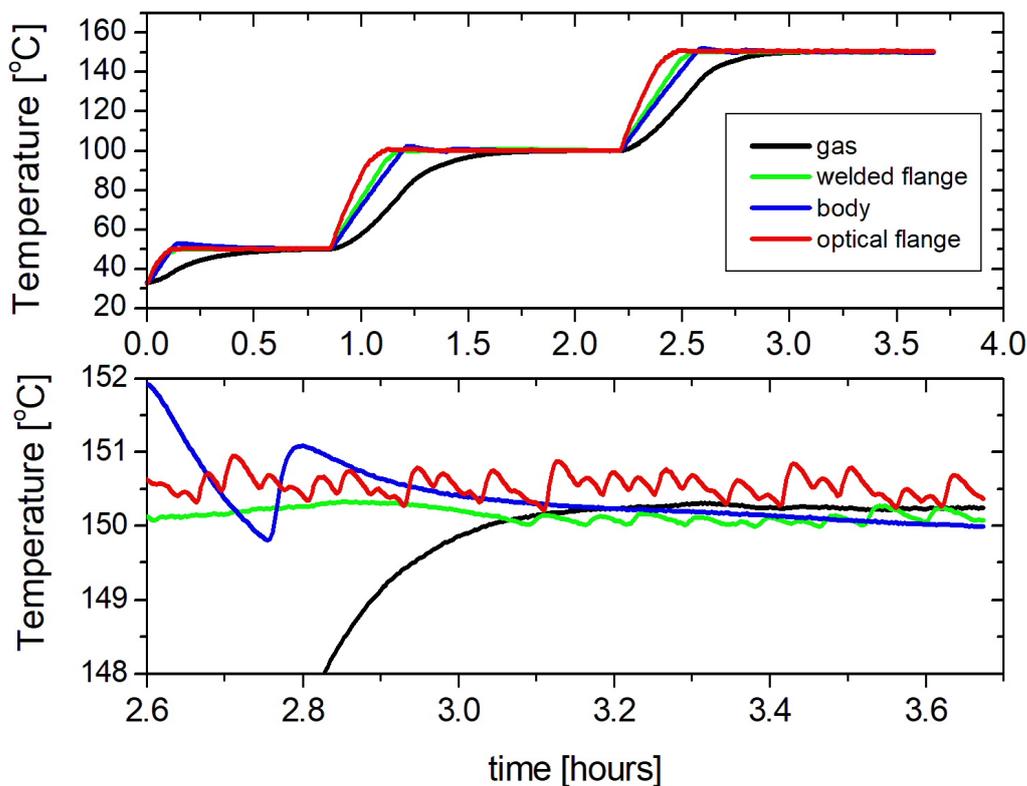
Figure 8. Upper panel: heating and temperature stabliaztion in three steps. Lower panel (enlarged part of the upper panel) : Temperature stability of the different parts of the cell and the gas during active stabilization.

The temperature of the cell has been also actively stabilized by using a PID feedback on the heaters. When the set point has been reached the power supply for each heater is controlled by a separate PID control which regulates the supplied power and switches the heaters on and off. This method is used for temperatures above ambient temperature. Figure 8 shows how the cell is heated in three steps and stabilized in temperature at 50, 100 and 150 °C. It can be observed that the temperatures of the

230 different parts of the cell are stabile within a few degrees once the PID regulation takes effect, while the gas temperature is reaching an even more stable temperature after 15 to 20 minutes. It can be observed that all parts of the cell are in excellent equilibrium and that the gas temperature is stable within ±0.5 degree or better. Active temperature stabilization below room temperature requires that the liquid nitrogen flow is always active to counteract the heating regulated by PID control. During cooling the liquid nitrogen flow is maximum until the preset temperature is reached and is reduced to maintain rougly the set

235 point. Fine tuning is obtained by regulating the four heaters by PID as explained before.

7.2 Tests of the FTS coupled to the multipass cell

The multipass cell mounted inside PASSxS is an open commercial White cell, with a base length of 20 cm. The effective optical path can be varied from a minimum of 0.8 m to a maximum of 9.6 m. Here we have aligned the cell with 16 passes before inserting it in PASSxS, corresponding with a 3.2 m pathlength. It should be noted that the coupling of the FTS to the

240 White cell is not straightforward, since the propagation of the focused light beam can not be observed once inside the two vacuum chambers. After an initial alignment with the visible light emitted by a HeNe laser, the transfer optics have been fine tuned to obtain a maximum output at the exit window.

The effective optical path length of the White cell inside the sample chamber (see Figure 5) has been verified by performing a measurement of a known quantity of carbondioxide and comparison with a spectral simulation. To this purpose

245 the sample cell has been filled with carbondioxide at a pressure of 4.3 bar at room temperature (294 K). For this measurement we used a MCT detector, a KBr beam splitter and a resolution of 2 cm^{-1}. Using a free on line tool for the simulation (https://spectra.iao.ru/en/en/mixt/spectr/) a synthetic spectrum was obtained. The results are shown in Figure 9, where the red curve refers to the measured spectrum while the black curve represents the simulation with an optical pathlength of 3.2 m. The excellent agreement between the two curves confirms that the optical pathlength is 3.2 m.

250 Furthermore several test measurements have been performed at different temperatures, recording absorption spectra of CO$_2$ involving both cooling and heating of the gas (see Figure 10).

8 Conclusions

A novel absorption cell for spectroscopy of planetary atmospheres has been designed, constructed and tested. The cell has shown to have an excellent passive thermal stability, remaining within 5 ° C of the set temperature in an hour of time. Active

255 temperature stabilization has also been demonstrated and a temperature stability of ± 1 degree, or better, on the time scale of one hour has been obtained.
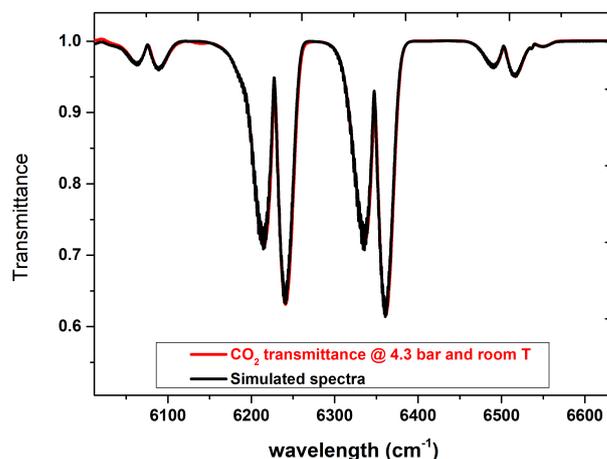
Figure 9. Comparison between acquired CO_2 spectra @ room temperature and 4.3 bar (red curve) and simulated (black curve)
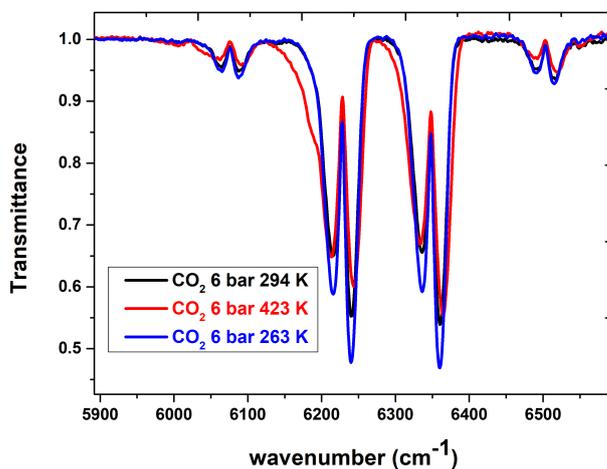
Figure 10. Carbondioxide absorption spectra at different temperatures and 6 bars of pressure.

A maximum heating rate of about 145 K/h has been observed while the cooling rate is about 30 K/h. A full temperature run from the lowest to the highest temperature in one day would require an overnight cooling to the lowest temperature, followed by a heating with a heating rate of about 60 K/h. A data acquistion of the Fourier Transform Spectrometer recording 100-200

260 scans at medium resolution, would allow to obtain a full spectrum at regular intervals of a few degrees.

We are planning to mount a resonant CRD cavity in PASSxS, in order to perform more sensitive absorption measurements for selected wavelengths.

Author contributions. GP and MS developed the concept of PASS*x*S. AB was responsible for the 3D design of the instrument. SS, GP, AB and DB took care of assembling, tests and PID development and implementation. SS performed all test measurements. MS prepared the

265   manuscript with contributions from all co-authors.

Competing interests. The authors declare that they have no conflict of interest.

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type of cell	pressure	temperature range	P.L [m]	window	Reference
cell in furnace	<4 atm	300 K < T < 1200 K	0.2	Al_2O_3	Abu-Romia and Tien (1966)
cell in furnace	<60 bar	291 K < T < 751 K	0.044	Al_2O_3	Hartmann and Perrin (1989)
cell in furnace	< 50 atm	300 K < T < 900 K	0.37	Al_2O_3	Rieker et al. (2007)
cell in furnace	< 200 bar	300 K < T < 650 K	0.02	ZnS	Stefani et al. (2013)
cell in furnace	< 100 bar	300 K < T < 1000 K	0.03	Al_2O_3	Christiansen et al. (2016)
cell in furnace	< 30 atm	300 K < T < 800 K	0.21	CaF_2	Almodovar et al. (2019)
cell in furnace	< 100 atm	300 K < T < 1200 K	0.37	CaF_2/Al_2O_3	Schwarm et al. (2019)
in vacuum cell	10 bar	87 K < T < 120 K	165	not specified	McKellar et al. (1970)
in vacuum cell	1 - 5 bar	190 K < T < 300 K	512	CaF_2	Ballard et al. (1994)
in vacuum cell	< 1 bar	120-300 K	2540		Horn and Pimentel (1971)
in vacuum cell	< 1bar	100-300 K	500		Briesmeister et al. (1978)
in vacuum cell	< 1 bar	160-300 K	40-1500		Kim et al. (1978)
in vacuum cell	< 10 atm	215-470 K	96	BaF$_2$/KBr	Shetter et al. (1987)
polystyrene	< 1 bar	123 K < T < 423 K	3	CaF_2	Schermaul et al. (1996)

Table 1. The Table lists some relevant properties of a number of coolable and heatable absorption cells reported in literature. The Table is not an exhaustive list of such cells, but is intended to give an example of what has been achieved in the past.

material	spectral transmission (nm)	index of refraction	maximum transmission	thickness (mm)	Hardness Knoop	thermal expansion coefficient $(10^{-6}\,\mathrm{K}^{-1})$	thermal conductivity $(\mathrm{Js}^{-1}\,\mathrm{m}^{-1}\,\mathrm{K}^{-1})$
BaF_2	150-12000	1.48	0.93	9.51	82	18.1	11.7
CaF_2	130-10000	1.43	0.94	8.16	178	18.8	9.7
NaCl	250-16000	1.54	0.91	31.75	18	40	6.5
ZnSe	500-16000	2.4	0.66	6.64	120	7.1	18
ZnS	370-13500	2.37	0.67	5.94	210	6.6	16.7
Sapphire	200-5000	1.77	0.85	2.33	2000	4.5	34.6
Si	1500-8000	3.46	0.39	4.41	1150	4.15	163.3
Fused silica	150-3200	1.46	0.93	7.1	600	0.55	1.5
Fused quartz	260-2500	1.46	0.93	7.1	600	0.55	1.3
BK7	350-2500	1.52	0.91	12.12	480	7.1	1.1
Borosilicate	350-2800	1.51	0.92	6.86	470	3.3	1.14

Table 2. The Table lists the most important optical, thermal and mechanical properties of a variety of optical window materials. The values reported should be taken as indicative values, since different values can be found in literature and in specifications of commercial optical materials.