O2 signature in thin and thick O2–H2O ices*,**

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ABSTRACT

Aims. In this paper we investigate the detectability of the molecular oxygen in icy dust grain mantles towards astronomical objects. Methods. We present a systematic set of experiments with O2–H2O ice mixtures designed to disentangle how the molecular ratio affects the O2 signature in the mid- and near-infrared spectral regions. All the experiments were conducted in a closed-cycle helium cryostat coupled to a Fourier transform infrared spectrometer. The ice mixtures comprise varying thicknesses from 8 µm to 300 µm. The absorption spectra of the O2–H2O mixtures are also compared to the one of pure water. In addition, the possibility to detect the O2 in icy bodies and in the interstellar medium is discussed. Results. We are able to see the O2 feature at 1551 cm−1 even for the most diluted mixture of H2O:O2 = 9:1, comparable to a ratio of O2/H2O = 10% which has already been detected in situ in the coma of the comet 67P/Churyumov-Gerasimenko. We can provide an estimate for the detection of O2 with the future mission of the James Webb Space Telescope (JWST).

Key words. astrochemistry – methods: laboratory: solid state – techniques: spectroscopic – ISM: molecules – infrared: ISM

1. Introduction

Astrochemical models have always dedicated special attention to molecular oxygen. With a cosmic abundance twice that of C, atomic O is the third most abundant element in space. In dense clouds, standard gas phase chemical models therefore suggest a comparable ratio of CO and O2 after times ≥ 3 × 105 yr (e.g. Woodall et al. 2007), where O2 is supposed to be formed especially via OH + O → O2 + H. The OH here can be formed by the dissociative recombinations of H2O+ → OH + 2H. However, observations with the Submillimeter Wave Astronomy Satellite (SWAS) by Goldsmith et al. (2000) towards Orion and with Odin by Larsson et al. (2007) towards ρ Oph showed a significant difference between model predictions and measurements. The O2 abundances found were more than 100 times smaller than those predicted by models (Goldsmith et al. 2000). Better agreement with observations can be obtained if freeze-out of O atoms onto dust grains is taken into account in gas-grain chemical models (Bergin et al. 2000; Viti et al. 2001), with consequent surface production of H2O and O2, which may trap a significant fraction of oxygen, leaving only some atomic O and CO in the gas phase. Observations conducted by Listau et al. (2012) led to a O2 column density of N(O2) = 5.5 × 1015 cm−2 with an upper limit of abundance of N(O2)/N(H2) = 5 × 10−8 in warm gas (T > 50 K) and to N(O2) = 6 × 1015 cm−2 with a little higher abundance in cold gas (T < 30 K). Listau et al. (2012) stated that detecting gas phase O2 might be so difficult because the O2 abundance is transient in ρ Oph A and O2 is no longer detectable after ~2 × 105 yr. A relatively large amount of O2 has only been found with Herschel in Orion as reported by Goldsmith et al. (2011). This source is quite warm (≥180 K), leading to a grain temperature of ≥100 K. At this temperature the grains are warm enough to desorb H2O ice and keep a large amount of oxygen with a big fraction in the form of O2 in the gas phase. Another explanation for the high O2 abundance found by Goldsmith et al. (2000) is that low-velocity C-shocks might be responsible for the increase of molecular oxygen in the gas phase.

In the gas phase, the formation of O2 via

OH + O → O2 + H,

has been discussed by for example, Davidsson & Stenholm (1990) and Carty et al. (2006). According to Ioppolo et al. (2011), O2 is formed in the solid state via

O + O → O2.

Possible other formation paths for molecular oxygen as suggested by Ioppolo et al. (2011) such as

HO2 + H → O2 + H2,

are still under discussion. With present CO molecules, Ioppolo et al. (2011) reports the formation of CO2 rather than O2. Also, the reaction HO2 + H → O2 + H2 can have a large activation barrier of 79.6 kJ mol−1 (Mousavi`Pou and Saheb 2007) which makes it unlikely to proceed at low temperature in gas phase. Reaction-diffusion competition, however, increases the probability of overcoming the reaction barrier on the ice surface (Herbst & Millar 2008). In the solid state, O2 is expected to form by the reaction of two O atoms, O + O → O2 (Tielens & Hagen

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** The raw spectra are only available at the CDS via anonymous ftp to cdsarc.u-strasbg.fr (130.79.128.5) or via http://cdsarc.u-strasbg.fr/viz-bin/qcat?J/A+A/620/A46

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to 10% relative to water has been found in the coma of the comet 67P/Churyumov-Gerasimenko, as Bieler et al. (2015) and Mousis et al. (2016) have recently reported. Successive work of Keeney et al. (2017) comparing line of sight measurements of O$_2$ conducted with the Alice far-ultraviolet spectograph on Rosetta with in situ measurements of the Rosetta Orbiter Spectrometer for Ion and Neutral Analysis (ROSINA) hint to even higher abundances of 11–68% with a mean value of 25%, although the comparison is not easily done. This detection opens new scenarios and raises interest in the possibility of detecting molecular oxygen in cometary and interstellar ice. Recent work by Taquet et al. (2016) show that solid O$_2$, with a molecular ratio to water ice similar to those measured in comet 67P, can be produced in molecular clouds with relatively low H to O abundance ratio in the gas phase, high densities ($\geq 10^5$ cm$^{-3}$) and dust temperature around 20 K, higher than that typically measured in interstellar dark clouds (10–15 K).

In this paper, we implement new laboratory experiments based on the work of Breukers (1991) as presented in Ehrenfreund et al. (1992), where the 6.45 $\mu$m molecular oxygen feature was measured in an ice mixture of H$_2$O:CO:CO$_2$:O$_2 = 2:2:0.5:1$ with unknown thickness. On the basis of this experiment, we have extended our analysis to different molecular composition ratios, as well as to different thicknesses. We have limited our analysis to the ice mixtures composed of H$_2$O and O$_2$ to study solely the impact of the water matrix on the imbedded O$_2$ feature, even though this molecular composition is not necessarily representative of the average composition of astrophysical ice. Thus, we put strong emphasis on the dependence of the ice composition on the O$_2$ band strength. Further studies with different mixtures, inclusive of CO and CO$_2$ at a 20–25% level, as found in interstellar ices (e.g. Boogert et al. 2015) will be presented in a future paper. This paper is structured as followed: We describe in Sect. 2 the methods and the setup used in the experiment. In Sect. 3 we present the experimental results and in Sect. 4 we discuss our measurements. Section 5 is dedicated to the astrophysical implications of our experiments.

2. Methods

The experiments were conducted in the recently developed cryogenic laboratory at the Center for Astrochemical Studies (Max Planck Institute for Extraterrestrial Physics) in Garching (Germany). The experimental setup is composed by a high power cryocooler, purchased from Advanced Research Systems (ARS), hosted in the sample compartment of a high resolution Bruker IFS 120/5HR Fourier Transform Infrared (FTIR) spectrometer.

The cryocooler consists of a cold finger situated into a vacuum chamber, with a final vacuum of $10^{-7}$ mbar. A sample holder (model SHO-1A, also from ARS) is placed at the end of the cold finger, suited to be cooled down to a minimum temperature of 4.2 K. The temperature is controlled by a Lake Shore Cryotronics (model 335) temperature controller, equipped with DT-670 Silicon Diodes sensors. The measured lowest temperature reached by the sample holder is 5 K. The sample holder can be complemented with substrates of different materials, on top of which the ices can be formed by condensation from the gas phase. The substrate used for this set of experiments is made of potassium bromide (KBr), which offers, with a transmission of $>90\%$ through the whole observed spectral range, the best optical properties in the desired frequency range. The appropriate gas mixture is introduced into the cryocooler by an expansion through a 6 mm stainless steel pipe, attached to a gas reservoir. The exit of the pipe is placed at a distance of approximately 2 cm
from the sample holder, facing the substrate. In this set of experiments the gas mixtures were deposited onto the substrate kept at a temperature of 10 K.

The vacuum chamber is complemented by two ZnSe optical windows, and one quartz window for visual inspection. For the measurements in the mid-infrared (MIR) and in the near-infrared (NIR) spectral regions, with a resolution of 2 cm$^{-1}$, a DTGS (deuterated triglycine sulphate) detector and a nitrogen cooled InSb detector, respectively, were used. A globar lamp was used as radiation source. A scheme of the arrangement of the cryocooler and its main components is illustrated in Fig. 1.

The gas mixtures were prepared in a 2 litre glass flask by using standard manometric techniques. The ratios of H$_2$O to the O$_2$ were adjusted by measuring the pressure inside the glass flask following the ideal gas law

\[ pV = nRT, \]

whereas the number of H$_2$O and O$_2$ particles is set by the isotherm relation

\[ \frac{n_i}{n_{tot}} = \frac{p_i}{p_{tot}} = \frac{V_i}{V_{tot}}, \]

where $n_i$ is the particle number, $p_i$ the partial pressure and $V_i$ the partial volume of the gas $i$, in our case H$_2$O and O$_2$. The total pressure $p_{tot}$ is the sum of all partial pressures $\sum p_i$, $n_{tot} = \sum n_i$ and $V_{tot} = \sum V_i$.

The gas mixture composition used for each experiment is outlined in Table 1. Distilled water that had been degassed in a freeze-pump-thaw cycle three times, and oxygen with a purity of 99.999% were introduced in the cooling chamber under high vacuum with a base pressure of 10$^{-6}$ mbar. The deposition time was varied starting with deposition times of 30 s, using a moderate deposition rate, and increasing the deposition time up to 3 min with fast deposition rate, so that thicknesses of 0.03 µm ($\sim$100 MLs) up to 3 µm ($\sim$10000 MLs), with an uncertainty of 20–30%, could be analysed. In the fourth column of Table 1, the water column density for thick ice reached after 1 min of deposition time for each ice mixture is listed; the derived water ice thickness and the oxygen column density are indicated in Cols. 5 and 6, respectively. We note that the latter has a high error for water rich ices due to limits in determining the area of the weak oxygen feature that is overlapped by the water bending vibration mode. Also, a comparison of $N_{H_2O}$ and $N_{O_2}$, to estimate the real ice composition is difficult for oxygen rich ices due to monomer and dimer features in the water bands.

The thickness of the deposited ice has been calculated from the area of the three bands characteristic of the water ice spectral signature. First, the column density $N$ has been estimated from the band area for the water component, following the relation

\[ N = \frac{\ln(10) \cdot \text{Area}}{A}, \]

and for $A$ using the band strength values from Hagen et al. (1981) and Gerakines et al. (1995). The factor ln(10) originates in the relation of the optical depth $\tau = \text{Abs} \cdot \ln(10)$ where Abs is the absorbance. $\tau$ is incorporated into the area. Then, the thickness $d$ (cm) has been calculated assuming

\[ d = \frac{N \cdot M}{\rho \cdot N_A}, \]

where $N$ is the column density (molecules cm$^{-2}$), $\rho$ the density (g cm$^{-3}$), $N_A$ the Avogadro constant (molecules mol$^{-1}$) and $M$ the molecular mass (g mol$^{-1}$). The total thickness has been estimated by considering the water to oxygen molecular ratio and scaling the thickness value accordingly. For this estimation we assumed that the ice molecular composition remains constant over the deposition time scale. There is no spectroscopic evidence which can prove that this assumption is correct, but assuming that the sticking coefficient is not varying significantly for the two components water and oxygen, we can estimate to produce a quite uniformly mixed ice. This is the general assumption used for this kind of experimental set-ups.

The cold KBr substrate is mounted with an angle of 45$^\circ$ with respect to the molecular beam direction. This configuration allows the deposition of the gas to take place simultaneously with the recording of the spectra. In the vacuum chamber, the molecules expand to a collisionless beam and the ice formed on the top of the substrate has a porous structure, with an expected density of approximately 0.8 g cm$^{-3}$ (Dohnálek et al. 2003; Snels et al. 2011). The thickness values provided for these experiments have been scaled to the direction normal to the substrate surface, to correct for the 45$^\circ$ angle of the substrate with respect to the spectroscopic path.

The measurements in our experimental setup work in transmittance and thus we would take an ice deposition on both sides of the substrate into account. Nevertheless, we experimentally confirm that ice was deposited on both sides of the substrate that faces the steel pipe. We used the laser interference method to ensure that no significant amount of ice is deposited on the substrate face opposite to the gas inlet.

3. Results

3.1. O$_2$ features in thin and thick ice samples

Figure 2 shows the whole observed spectrum for the different composition ratios after same deposition time. The figure clearly shows the H$_2$O stretching mode at 3280 cm$^{-1}$, the H$_2$O combination mode at 2200 cm$^{-1}$, the H$_2$O bending mode at 1660 cm$^{-1}$ and the H$_2$O libration mode at 760 cm$^{-1}$. Moreover, the O$_2$ feature can be found at 1551 cm$^{-1}$. In spectra #2, #6, #7, and #8, features due to CO$_2$ contamination are present at 2343 cm$^{-1}$ and at 660 cm$^{-1}$. The H$_2$O:O$_2$ = 2:1 spectrum shows the saturation of the stretching mode because of different deposition conditions compared to the other experiments.
Fig. 2. Spectra of all H$_2$O–O$_2$ composition ratios for thick ice with same deposition time of 1 min each. The number of H$_2$O monolayers here goes from 80 ML (thickness $\approx$ 0.03 $\mu$m) for H$_2$O:O$_2$ = 1:9 to 1900 ML (thickness $\approx$ 0.68 $\mu$m) for H$_2$O:O$_2$ = 9:1. The spectra for the different compositions are shifted in the absorbance scale for helping their visualization. The vertical red dashed line indicates the O$_2$ band position at 1551 cm$^{-1}$.

Table 1. Gas mixture composition, expressed as partial pressure ratio, the water column density ($N_{H_2O}$), the water ice thickness ($d_{H_2O}$) and O$_2$ column density ($N_{O_2}$) after a total deposition time of 1 min for thick ice for each experiment presented in this paper.

| Exp | H$_2$O | O$_2$ | $N_{H_2O}$/10$^{18}$ mol cm$^{-2}$ | $d_{H_2O}$ (µm) | $N_{O_2}$/10$^{18}$ mol cm$^{-2}$ |
|-----|--------|------|-----------------------------------|----------------|----------------------------------|
| #1  | 9      | 1    | 1.94                              | 0.68           | 0.02                             |
| #2  | 4      | 1    | 1.42                              | 0.50           | 0.02                             |
| #3  | 3      | 1    | 1.12                              | 0.39           | 0.07                             |
| #4  | 2      | 1    | 2.17                              | 0.77           | 0.21                             |
| #5  | 1      | 1    | 0.95                              | 0.33           | 0.28                             |
| #6  | 1      | 2    | 0.58                              | 0.21           | 0.16                             |
| #7  | 1      | 4    | 0.25                              | 0.09           | 0.32                             |
| #8  | 1      | 9    | 0.08                              | 0.03           | 0.25                             |

Notes. The uncertainty for $N_{H_2O}$ and $d_{H_2O}$ lie within 20–30%.

In the thick ice layer regime (estimated thicknesses ranging between 1 and 3 µm) the oxygen feature is visible at all the investigated molecular ratio. Our limit cases are the mixture in excess of water (experiment #1) and the mixture in excess of oxygen (experiment #8). It is convenient to divide the analysis into two parts, one for the experiments from #1 to #4, and a second for the experiments from #5 to #8. In the first part, excess of water at different molecular ratios is investigated. In these experiments, the oxygen feature is overlapped to the bending vibration mode of water, making its detection increasingly difficult as the water becomes predominant in the molecular ratio (cf. Fig. 3). Nevertheless, even with a water to oxygen ratio of 9:1, the oxygen feature is still visible in our recorded spectrum, as it shown in Fig. 3.

For the thin ice, we conducted separate experiments in order to monitor the dependence of the O$_2$ band position on the physical conditions of the thin ice. The spectrum of the thin H$_2$O:O$_2$ = 2:1 ice (thickness 0.022–0.053 µm) is shown enclosed around 1660 cm$^{-1}$ in Fig. 4. Presenting even thinner ice, Fig. 5 shows the first three deposition steps (thickness 0.008–0.022 µm) in order to enhance the visibility of the O$_2$ feature of which we see hints of the band at 1551 cm$^{-1}$ also for the thinnest ice. The water bands assume the characteristic features of water trapped in a matrix, as can be observed from Ehrenfreund et al. (1996).

In the experiments in excess of oxygen, the O$_2$ feature is progressively isolated from the water bending feature. Its spectral characteristics, though, are not varying significantly with the change in the H$_2$O to O$_2$ ratio, in terms of frequency shift and band profile. Therefore, these spectra offer the best conditions for the estimate of the O$_2$ band strength. The band strength $A$ is given as

$$A = \int \sigma(\tilde{\nu})d\tilde{\nu} = \frac{1}{N} \int r(\tilde{\nu})d\tilde{\nu},$$

(5)

where $\sigma(\tilde{\nu})$ is the cross-section (cm$^2$) and $r(\tilde{\nu})$ the optical depth for a given wavenumber $\tilde{\nu}$ (cm$^{-1}$). Using

$$r = \text{Abs} \cdot \ln(10),$$

(6)

where Abs is the measured absorbance of the O$_2$ feature, we get

$$\int r(\tilde{\nu})d\tilde{\nu} \approx \text{Abs} \cdot \ln(10) \cdot d\tilde{\nu}.$$  

(7)

We measured $d\tilde{\nu} = 10$ cm$^{-1}$ and for O$_2$ the column density $N = 3.01 \times 10^{22}$ mol cm$^{-3}$ d. The derived band strengths for the
Fig. 3. Magnification of spectra of Fig. 2 around the O\textsubscript{2} feature (marked by the vertical red dashed line) for all H\textsubscript{2}O–O\textsubscript{2} mixtures for thick ice.

Fig. 4. Magnified spectra of H\textsubscript{2}O:O\textsubscript{2} = 2:1 mixture around the O\textsubscript{2} feature; the ice thicknesses is between 0.022 and 0.053 \(\mu\)m for thin ice.

Fig. 5. Magnified spectra of H\textsubscript{2}O:O\textsubscript{2} = 2:1 mixture around the O\textsubscript{2} feature; the thicknesses is between 0.008 and 0.022 \(\mu\)m for thin ice.

different ice mixtures and a comparison with the values found by Ehrenfreund et al. (1992) can be found in Table 2.

For comparable experiments, where the values of H\textsubscript{2}O/O\textsubscript{2} presented in this work are equal to those presented by Ehrenfreund et al. (1992), the values of the band strength agree with a factor of approximately two. This difference is most likely due to the influence of CO and CO\textsubscript{2} in the experiments conducted by Ehrenfreund et al. (1992), which enhance the oxygen band strength.

As the feature of solid O\textsubscript{2} is present at 1551 cm\textsuperscript{-1}, there exists the possibility for observable overtones in the NIR. While we don’t expect to see any O\textsubscript{2} features near 3102 cm\textsuperscript{-1} (3.22 \(\mu\)m) due to the strong water signal, we looked for the next possible overtone at 4653 cm\textsuperscript{-1} (2.15 \(\mu\)m). Even, for the thick ice with 3 \(\mu\)m thickness, there is no O\textsubscript{2} feature to be found near 4653 cm\textsuperscript{-1}.

3.2. Dangling bonds

We note that in our experiments we dealt with a porous amorphous ice structure. For this reason, in the recorded spectra we observe the features assigned to the presence of the so-called dangling bonds, that is, features arising from the OH stretching vibration of water molecules that are not engaged in an intermolecular interaction with the ice bulk. Although the analysis of the spectral signature of the dangling bonds is not directly applicable to the comparison with astronomical observations, for which no detection is currently available, we believe that studying the way in which the presence of oxygen affects the features ascribed to the dangling bonds can provide useful information for future laboratory experiments. In Fig. 6 the spectral region of the dangling bonds for thick ice corresponding to the different H\textsubscript{2}O–O\textsubscript{2} mixtures and the pure water is shown. The increasing steepness of the spectra towards 3500 cm\textsuperscript{-1} relate to the increasing ratio of H\textsubscript{2}O–O\textsubscript{2} as the stretch feature of water rises in intensity with increasing water abundance. The positions of the dangling bond features can be found in Table 3.

Figure 6 shows a red shift of the dangling bonds peaks going from the pure water to the H\textsubscript{2}O:O\textsubscript{2} = 2:1 mixture, from 3697 cm\textsuperscript{-1} (2.705 \(\mu\)m) and 3683 cm\textsuperscript{-1} (2.715 \(\mu\)m) to 3698 cm\textsuperscript{-1}.
Fig. 6. Thick-ice absorption spectrum of H$_2$O:O$_2$ mixtures compared to pure water. To enable a better overview, similar to Fig. 2, the spectra of the different mixtures have been shifted.

Table 2. Band strength (A) of O$_2$ for the different ice compositions.

| Mixture$^b$ | Ratio$^b$ | A$^b$ (cm mole$^{-1}$) |
|------------|-----------|-------------------------|
| H$_2$O : CO : CO$_2$ : O$_2$ 2 : 2 : 0.5 : 1 | 1.0e–19 |
| H$_2$O : CO : O$_2$ 1 : 1 : 1 | 0.7e–19 |
| CO : O$_2$ 1 : 1 | 0.7e–19 |
| CO$_2$ : O$_2$ 10 : 1 | 3.0e–18 |

Notes. ($^a$) The values have been averaged for the analysis of different ice thicknesses. ($^b$) Comparison with band strength as derived by Ehrenfreund et al. (1992). H$_2$O to O$_2$ ratios with equal values to those used in our work have been aligned to facilitate comparison.

Table 3. Gas mixture composition and position of the dangling bonds (with shoulder feature position where present) for each experiment presented in this paper.

| Exp | H$_2$O : O$_2$ | Dang. bond #1 (shoulder)/cm$^{-1}$ | Dang. bond #2 (shoulder)/cm$^{-1}$ |
|-----|---------------|------------------------------------|------------------------------------|
| #1  | 9 : 1         | 3717                               | 3698                               |
| #2  | 4 : 1         | 3689                               | 3669                               |
| #3  | 3 : 1         | 3698                               | 3678                               |
| #4  | 2 : 1         | 3693                               | 3678                               |
| #5  | 1 : 1         | 3731 (3725)                        | 3699 (3680)                        |
| #6  | 1 : 2         | 3731 (3727)                        | 3699 (3686)                        |
| #7  | 1 : 4         | 3731 (3727)                        | 3699 (3685)                        |
| #8  | 1 : 9         | 3731 (3725)                        | 3699 (3680)                        |

(2.704 µm) and 3678 cm$^{-1}$ (2.719 µm). The change in the spectroscopic feature of the dangling bonds for the water and oxygen ices with respect to pure water ice is in agreement with previous experiments performed by Palumbo et al. (2010), in which the effect on the profile of the dangling bond feature for an ice mixture of approximately 20% of oxygen in water is reported. Their study can be compared to our H$_2$O:O$_2$ = 4:1 mixture. For oxygen-rich ice mixtures, the peak shape and position is probably influenced by the presence of water monomers and dimers embedded in the oxygen matrix, as reported in Ehrenfreund et al. (1996).

4. Discussion

We decided to limit our study to the case of the molecular oxygen complexes with water and to extend the amount of molecular ratio explored going from ice mixtures in excess of water to excess of oxygen, in order to have a complete overview of the molecular oxygen signature in different astrophysical environments. Furthermore, for each experiment we have analysed the IR spectra in the thin and thick ice layer regimes, showing that the oxygen spectral signature does not exhibit different characteristics, in terms of band position and shape, with respect to the two approaches. The molecular vibration of O$_2$ by
itself is inactive in the infrared since the dipole moment doesn’t change upon molecular vibration. Nevertheless, the interaction with the water matrix breaks the electron symmetry and induce a small dipole moment, which allows for the detection in the IR region.

In the thin ice layer regime, in which the thicknesses of the ice layer (estimated for the water component) varys between 0.008 and 0.053 μm, the oxygen feature has been observed only in the most favourable case, that is, the H$_2$O:O$_2$ = 2:1 mixture (experiment #4). In this molecular ratio, the band strength of the oxygen feature is enhanced, as shown by Ehrenfreund et al. (1992), the instrumental detection limit in dealing with a low column density is overcome, and the observation of a low intensity band is possible. For even thinner ices however, we don’t expect the shape and position of the O$_2$ feature to change much, but the detection of O$_2$ depends on the total column density, so in the end it depends on the ice thickness as well as dust number density. In the remaining cases the low intensity of the band signal did not allow for a detection. The frequency position measured in the experiment #4 is 1551 cm$^{-1}$ (6.45 μm). In order to increase the S/N for the thin H$_2$O:O$_2$ = 2:1, the recording of the spectra was performed with a higher number of recorded cycles (2048 record cycles; for comparison: 1184 record cycles for thick ice). That way, the noise was reduced in order to obtain a S/N ≤ 3 even for the thinnest ice.

In addition, we compared the dangling bond features of pure water with that of the H$_2$O:O$_2$ = 9:1 mixtures. As already observed by Palumbo et al. (2010), the profile of the dangling bond feature depends on the presence of other species mixed-in with water ice. The presence of oxygen affects the dangling bonds profile in term of intensity and shape. Their profile may be related to the microstructure of the deposited ice. As can be observed from Fig. 6, the H$_2$O:O$_2$ ratio in the ice is affecting significantly the spectral characteristic of the water dangling bonds. Going from the water rich to oxygen rich mixtures, we observe a progressive change in the relative intensity of the two main features and a shift in their position. For oxygen rich mixtures, we observe a predominant sharper feature at lower frequencies, while the water rich mixtures exhibit a smoother profile and similar relative intensities of the two components. The mixture with a similar water to oxygen ratio shows a profile which is in between the extremes. From this consideration we can relate the shape of the dangling bonds bands with the molecular composition of the bulk ice, allowing an identification of the enrichment of the ice in one or the other species. However, a detailed analysis of the effect of the structure of the ice on the dangling bond characteristic is outside the scope of this work.

Figure 7 shows the behaviour of the O$_2$ feature upon heating. Observed O$_2$ features started to vanish when the probes were heated to 35 K. At this temperature, the O$_2$ molecules trapped on the amorphous water ice matrix start to evaporate (cf. Bar-Nun et al. 1987). At a temperature of 50 K, the O$_2$ features were completely absent. Above this temperature the O$_2$ is not trapped by the porous amorphous solid water any more and the O$_2$ is desorbed from the deposited ice. This observation is consistent with the experiments conducted by Ayotte et al. (2001).

5. Astrophysical implications

Our experimental approach intends to explore astrophysical scenarios. The experiments dedicated to the thin ice layer regime (number of monolayers < 150; counted using the thickness and density of the ice) simulate the conditions in the dense interstellar medium more adequately (Öberg, 2016), while the experiments in the thick layer regime attempt to extend the physical conditions relative to the centre of pre-stellar cores as well as in the midplane of protoplanetary disks, where pebbles and icy bodies precursors of comets and planetesimals with ice thicknesses >200 ML form (e.g. Bieler et al. 2015). There is a lack of observational data proving the presence of molecular oxygen in ISM ice, while O$_2$ has been recently detected in the coma of the comet 67P/Churyumov-Gerasimenko (Bieler et al. 2015; Mouissis et al. 2016).

Our experimental data show that the detection of the O$_2$ feature in thin ices is much more difficult compared to the thick ones, and the only molecular composition allowing the laboratory detection is the H$_2$O:O$_2$ = 2:1, which is unrealistic for the ISM ice composition. However, predictions by astrochemical models for pre-stellar cores, such as L1544, indicate that the icy mantles can reach thicknesses close to the thick ice regime in these experiments (e.g. Vasyunin et al. 2017). On the other hand, the mixture with a molecular ratio H$_2$O:O$_2$ = 9:1 will account for a realistic proportion like it was observed in the cometary coma of 67P/Churyumov-Gerasimenko with a mean value of 3.80 ± 0.85%.

5.1. Chemical modelling

We studied which ice structure and composition is predicted by current astrochemical models, and how it is related to the observational data on O$_2$:H$_2$O ratio and ice thickness. For this purpose, we used results from Vasyunin et al. (2017). Briefly, this is a three-phase (gas-reactive ice surface – (less) reactive ice bulk) dependent astrochemical model that includes an extensive set of gas-phase and grain-surface chemistry. In Vasyunin et al. (2017), the model has been successfully applied to the explanation of observed distribution of complex organic molecules (COMs) in the prototypical pre-stellar core L1544. The authors find that the best agreement between the model and the observed data is reached after 1.6 × 10$^5$ years of chemical evolution of a static cloud with physical structure similar to one reproduced for L1544. The model also reproduced the enhanced abundances of COMs at the so-called methanol peak located ~4000 AU (~0.015 pc) away from the centre of the core (the peak of the dust emission), as observed by Bizzocchi et al. (2014).

At the time of maximum O$_2$/H$_2$O abundance, the modelled ice thickness is 70 monolayers, but it is growing with time, and stabilizes at the methanol peak at 200 monolayers after 10$^5$ years of
evolution, as shown in Fig. 8. As such, we believe that modelling results are in rough agreement with observed values for O$_2$/H$_2$O in the coma of 67P/Churyumov-Gerasimenko comet. Also, the modelling suggests that icy mantles in pre-stellar cores such as L1544 are relatively thick, and may reach several hundreds of monolayers. Finally, it is interesting to note that while the model by Vasyunin et al. (2017) predicts gas-phase O$_2$ abundance, at the time of the best agreement between the model and observed values of COMs, to be at least an order of magnitude lower than that of CO, the O$_2$ gas-phase abundance is still overestimated by an order of magnitude in comparison to observed upper limits in other environments (e.g. Goldsmith et al. 2000). The gas-phase O$_2$ abundance in the model by Vasyunin et al. (2017) is mainly controlled by the reactive desorption mechanism, whose efficiency under various conditions is currently a matter of debate.

5.2. Astronomical observability

Using absorbance and thickness data obtained in our experiments, we were able to calculate the absorption coefficient

$$\alpha = \frac{\text{Abs} \cdot \ln(10)}{d},$$

for the different mixture ratios of O$_2$/H$_2$O. $\alpha$ as a function of the O$_2$/H$_2$O ratio can be found in Fig. 9. The absorption coefficients for water are in good agreement with the derived values from Warren & Brandt (2008), considering a discrepancy in sample temperature, while we have no possibility to compare the calculated absorption coefficient for O$_2$ with the literature. In order to calculate $\alpha$ for all O$_2$–H$_2$O ratios, the data were fit using two
different methods for statistical comparison. The first method
creates the fit by minimizing the $\chi^2$-error statistics. The second
method uses the least absolute deviation method that minimizes
the sum of absolute errors.

The calculated values were then used to derive the optical
depth and the transmittance of L1544 using the model by
Vasyunin et al. (2017) introduced in Sect. 5.1 (cf. Fig. 10). The
transmittance of an area with a constant absorption coefficient
can be calculated with

$$T = \frac{F}{F_0} = e^{-\tau \alpha s} = e^{-\tau},$$

where $F_0$ is the initial flux density received from the medium,
$F$ is the flux density transmitted by the medium, $s$ is the size of
the area with a certain absorption coefficient $\alpha$. For our calcu-
lations, we divide the modelled cloud into subpaths $s_n$ of constant
absorption coefficients and obtain

$$\tau_{\text{tot}} = \sum s_n \tau_{s_n}.$$  \hspace{1cm} (10)

Following this, we get the total transmittance

$$T_{\text{tot}} = \prod s_n \tau_{s_n}. \hspace{1cm} (11)$$

The optical depth and transmittance was computed only for the
inner part of our modelled L1544 where $O_2/H_2O > 10^{-6}$. The
derived optical depth and transmittance for the different H2O and
$O_2$ can be found in Table 4.

| Band      | $\tau$ (fitting method a) | $\tau$ (fitting method b) | $T$ (fitting method a) | $T$ (fitting method b) |
|-----------|--------------------------|--------------------------|------------------------|------------------------|
| 3280 cm$^{-1}$ | 0.625 ± 0.006          | 0.611 ± 0.039          | 0.535 ± 0.005        | 0.543 ± 0.039        |
| 2200 cm$^{-1}$ | 0.017 ± 0.001          | 0.018 ± 0.002          | 0.982 ± 0.052        | 0.982 ± 0.093        |
| 1660 cm$^{-1}$ | 0.056 ± 0.002          | 0.055 ± 0.003          | 0.945 ± 0.024        | 0.946 ± 0.048        |
| 1551 cm$^{-1}$ | 7.4 × 10$^{-4}$ ± 8.1 × 10$^{-4}$ | 1.0 × 10$^{-5}$ ± 3.0 × 10$^{-6}$ | 0.999 ± 0.110 | 1.000 ± 0.337        |
| 760 cm$^{-1}$  | 0.140 ± 0.003          | 0.139 ± 0.006          | 0.869 ± 0.016        | 0.870 ± 0.035        |

6. Conclusions
This paper presents spectral features of solid molecular oxygen
enclosed in a water matrix. The analysis is compared to previous
studies reported by Ehrenfreund et al. (1992) and Palumbo et al.
(2010), and extended to further molecular ratios and ice thick-
nesses, as motivated by the recent detection of $O_2$ in the comet
67P/Churyumov-Gerasimenko. In particular, we have explored
the possibility of detecting $O_2$ in solid form towards pre-stellar
cores for which gas-grain chemical model predictions were
available.

In our experiments, $O_2$ is found at 1551 cm$^{-1}$ for thick ice. Also,
we find evidence for the $O_2$ band at that position even for our
thinnest ice. Because of their more heterogeneous composi-
tion, interstellar ices may, however, show the $O_2$ features around
these values. The porous amorphous nature of the ice mixture
produces the dangling bonds near the stretching mode of water.
However, while their position and intensity depends on the ratio
of H2O and $O_2$, the lack of detection in space hint to the conclu-
sion that the ice there is compact and not porous (e.g. Palumbo
2005). The $O_2$ feature can only be seen for temperatures ≤35 K.

The behaviour of the dangling bonds in dependence of the
ice mixture composition has been discussed. The $O_2$/$H_2O$ ratio
not only has an effect on the intensity of the features but also on
their position and shape. This is especially so for mixtures with
an excess of $O_2$ that show a shoulder feature or even a second
maximum near the two main bands.

The three-phase time-dependent astrochemical model of the
pre-stellar core L1544, as introduced by Vasyunin et al. (2017)
predicts thick ice (>200 ML) and $O_2$/$H_2O$ fractions close to
those measured towards the comet 67P. Using JWST, it is not
feasible to detect $O_2$ in solid phase via measuring the transmis-
sion ratio of L1544 using the MIRI instrument. New estimates for
the $O_2$ detection in mixed ices with JWST, however, will be
done in a future paper.

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