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Deep observations of O\textsubscript{2} toward a low-mass protostar with Herschel-HIFI\textsuperscript{*},\textsuperscript{**,\textsuperscript{***}}

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ABSTRACT

Context. According to traditional gas-phase chemical models, O\textsubscript{2} should be abundant in molecular clouds, but until recently, attempts to detect interstellar O\textsubscript{2} line emission with ground- and space-based observatories have failed. Aims. Following the multi-line detections of O\textsubscript{2} with low abundances in the Orion and \rho\textsubscript{Oph} A molecular clouds with Herschel, it is important to investigate other environments, and we here quantify the O\textsubscript{2} abundance near a solar-mass protostar. Methods. Observations of molecular oxygen, O\textsubscript{2}, at 487 GHz toward a deeply embedded low-mass Class 0 protostar, NGC 1333-IRAS 4A, are presented, using the Heterodyne Instrument for the Far Infrared (HIFI) on the Herschel Space Observatory. Complementary data of the chemically related NO and CO molecules are obtained as well. The high spectral resolution data are analysed using radiative transfer models to infer column densities and abundances, and are tested directly against full gas-grain chemical models. Results. The deep HIFI spectrum fails to show O\textsubscript{2} at the velocity of the dense protostellar envelope, implying one of the lowest abundance upper limits of O\textsubscript{2}/H\textsubscript{2} at \lesssim 6 \times 10^{-9} (3\sigma). The O\textsubscript{2}/CO abundance ratio is less than 0.005. However, a tentative (4.5\sigma) detection of O\textsubscript{2} is seen at the velocity of the surrounding NGC 1333 molecular cloud, shifted by 1 km s\textsuperscript{-1} relative to the protostar. For the protostellar envelope, pure gas-phase models and gas-grain chemical models require a long pre-collapse phase (\sim 0.7–1 x 10\textsuperscript{6} years), during which atomic and molecular oxygen are frozen out onto dust grains and fully converted to H\textsubscript{2}O, to avoid overproduction of O\textsubscript{2} in the dense envelope. The same model also reproduces the limits on the chemically related NO molecule if hydrogenation of NO on the grains to more complex molecules such as NH\textsubscript{2}OH, found in recent laboratory experiments, is included. The tentative detection of O\textsubscript{2} in the surrounding cloud is consistent with a low-density PDR model with small changes in reaction rates. Conclusions. The low O\textsubscript{2} abundance in the collapsing envelope around a low-mass protostar suggests that the gas and ice entering protoplanetary disks is very poor in O\textsubscript{2}.

Key words. astrochemistry – stars: formation – ISM: molecules – ISM: individual objects: NGC 1333 IRAS 4A

1. Introduction

Even though molecular oxygen (O\textsubscript{2}) has a simple chemical structure, it remains difficult to detect in the interstellar medium after many years of searches (Goldsmith et al. 2011, and references therein). Oxygen is the third most abundant element in the Universe, after hydrogen and helium, which makes it very important in terms of understanding the formation and evolution of the chemistry in astronomical sources.
Pure gas-phase chemistry models suggest a steady-state abundance of $X(O_2) = 7 \times 10^{-7}$ relative to $H_2$ (e.g., Table 9 of Woodall et al. 2007), however observations show that the abundance is several orders of magnitude lower than these model predictions. Early (unsuccessful) ground-based searches of $O_2$ were done through the $^{16}$O$^{18}$O isotopologue (Goldsmith et al. 1985; Pagani et al. 1993), for which some of the lines fall in a transparent part of the atmosphere. Due to the oxygen content of the Earth’s atmosphere, it is however best to observe $O_2$ from space. Two previous space missions, the Submillimeter Wave Astronomy Satellite (SWAS; Melnick et al. 2000) and the Odin Satellite (Nordh et al. 2003) were aimed at detecting and studying interstellar molecular oxygen through specific transitions. SWAS failed to obtain a definitive detection of $O_2$ at 487 GHz toward nearby clouds (Goldsmith et al. 2000), whereas $Odin$ observations of $O_2$ at 119 GHz gave upper limits of $\lesssim 10^{-7}$ (Pagani et al. 2003), except for the $\rho$ Ophiuchi A cloud ($X(O_2) \sim 5 \times 10^{-8}$; Larsson et al. 2007).

The Herschel Space Observatory provides much higher spatial resolution and sensitivity than previous missions and therefore allows very deep searches for $O_2$. Recently, Herschel-HIFI provided firm multi-line detections of $O_2$ in the Orion and $\rho$ Oph A molecular clouds (Goldsmith et al. 2011; Liseau et al. 2012). The abundance was found to range from $X(O_2) \approx 10^{-6}$ (in Orion) to $X(O_2) \approx 5 \times 10^{-8}$ (in $\rho$ Oph A). The interpretation of the low abundance is that oxygen atoms are frozen out onto grains and transformed into water ice that cools interstellar dust, leaving little atomic O in the gas to produce $O_2$ (Bergin et al. 2000). So far, $O_2$ has only been found in clouds where (external) starlight has heated the dust and prevented atomic O from sticking onto the grains and being processed into $H_2O$ as predicted by theory (Hollenbach et al. 2009) or where $O_2$ is enhanced in postshock gas (Goldsmith et al. 2011). Not every warm cloud has $O_2$, however. Melnick et al. (2012) report a low upper limit on gaseous $O_2$ toward the dense Orion Bar photon-dominated region (PDR).

Although the detection of $O_2$ in some molecular clouds is significant, these data tell little about the presence of $O_2$ in regions where solar systems may form. It is therefore important to also make deep searches for $O_2$ near solar-mass protostars to understand the origin of molecular oxygen in protoplanetary disks and eventually (exo-)planetary atmospheres. Even though the bulk of the $O_2$ in the Earth’s atmosphere arises from microorganisms, the amount of $O_2$ that could be delivered by cometary impacts needs to be quantified. In the present paper, a nearby low-mass deeply embedded protostar, NGC 1333 IRAS 4A, is targeted, which has one of the highest line of sight hydrogen column densities of $N(H_2) \sim 10^{24}$ cm$^{-2}$ derived from dust modeling (Jørgensen et al. 2002; Kristensen et al. 2012). Since the Herschel beam size at 487 GHz is a factor of ~6 smaller than that of SWAS, Herschel is much more sensitive to emission from these compact sources. Protostars also differ from dense clouds or PDRs by the fact that a significant fraction of the dust is heated internally by the protostellar luminosity to temperatures above those needed to sublimate O and $O_2$.

NGC 1333 IRAS 4A is located in the southeast part of the NGC 1333 region, together with IRAS 4B (henceforth IRAS 4A and IRAS 4B). A distance of $235 \pm 18$ pc is adopted based on VLBI parallax measurements of water masers in the nearby source SVS 13 (Hirota et al. 2008). Both objects are classified as deeply-embedded Class 0 low-mass protostars (André & Montmerle 1994) and are well-studied in different molecular lines such as CO, SiO, H$_2$O and CH$_3$OH (e.g., Blake et al. 1995; Lefloch et al. 1998; Bottinelli et al. 2007; Yildiz et al. 2012; Kristensen et al. 2010). Figure 1 shows a CO $J = 6$–5 contour map obtained with APEX (Yildiz et al. 2012) overlaid on a Spitzer/IRAC1 (3.6 µm) image (Gutermuth et al. 2008). Both IRAS 4A and IRAS 4B have high-velocity outflows seen at different inclinations. The projected separation between the centers of IRAS 4A and IRAS 4B is 31″ (~7300 AU). The source IRAS4A was chosen for the deep $O_2$ search because of its chemical richness and high total column density. In contrast to many high-mass protostars, it has the advantage that even very sensitive spectra do not show line confusion.

On a larger scale, early millimeter observations of CO and $^{13}$CO $J = 1$–0 by Loren (1976) and Liseau et al. (1988) found two (possibly colliding) clouds in the NGC 1333 region, with velocities separated by up to 2 km s$^{-1}$. Černis (1990) used extinction mapping in the NGC 1333 region to confirm the existence of two different clouds. The IRAS 4A protostellar envelope is centered at the lower velocity around $V_{LSR} = 7.0$ km s$^{-1}$, whereas the lower (column) density cloud appears around $V_{LSR} = 8.0$ km s$^{-1}$. The high spectral resolution of our data allows $O_2$ to be probed in both clouds. Optically thin isotopologue data of $^{16}$O$^{18}$O $J = 1$–0 up to $J = 5$–4 are used to characterize the conditions in the two components. Note that these velocities do not overlap with those of the red outflow lobe, which start at $V_{LSR} = +10.5$ km s$^{-1}$.

We present here the first sensitive observations of the O$_2$ 33–12 487 GHz line towards a deeply embedded low-mass Class 0 protostar, observed with Herschel-HIFI. Under a wide range of conditions, the O$_2$ line at 487 GHz is the strongest, therefore this line is selected for long integration. The data are complemented by ground-based observations of CO isotopologues and NO using the IRAM 30 m and JCMT telescopes. The CO data are used to characterize the kinematics and physical conditions in the clouds as well as the column of gas where CO is not frozen out. Since the O$_2$ ice has a very similar binding
energy as the CO ice, either in pure or mixed form (Collings et al. 2004; Acharyya et al. 2007), CO provides a good reference for O₂. NO is chosen because it is a related species that could help to constrain the chemistry of O₂. In the gas, O₂ can be produced from atomic O through the reaction (Herbst & Klemperer 1973; Black & Smith 1984)

\[ \text{O + OH} \rightarrow \text{O}_2 + \text{H} \]

with rate constants measured by Carty et al. (2006). The nitrogen equivalent of Eq. (1) produces NO through

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The outline of the paper is as follows. Section 2 describes the observations and the telescopes where the data were obtained. Results from the observations are presented in Sect. 3. The deep HIFI spectrum reveals a non-detection of O₂ at the velocity of the central protostellar source. However, a tentative (4.5 ± 0.5) km s⁻¹ emission as the CO ice, either in pure or mixed form (Collings et al. 2004; Acharyya et al. 2007), CO provides a good reference for O₂. NO is chosen because it is a related species that could help to constrain the chemistry of O₂. In the gas, O₂ can be produced from atomic O through the reaction (Herbst & Klemperer 1973; Black & Smith 1984)

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The molecular lines observed towards the IRAS 4A protostar (3₂⁻1⁻, +3₁⁻3¹,3⁻3⁰⁺ (J2000); Jørgensen et al. 2009) are presented in Table 1 with the corresponding frequencies, upper level energies (E_u/k_B), and Einstein A coefficients. The O₂ data were obtained with the Heterodyne Instrument for the Far-Infrared (HIFI; de Graauw et al. 2010) onboard the Herschel Space Observatory (Pilbratt et al. 2010), in the context of the “Herschel Oxygen Project” (HOP) open-time key program, which aims to search for O₂ in a range of star-forming regions and dense clouds (Goldsmith et al. 2011). Single pointing observations at the source position were carried out on operation day OD 445 on August 1 and 2, 2010 with Herschel obsids of 1342202025—.1342202032. The data were taken in dual-beam switch (DBS) mode using the HIFI band 1a mixer with a chop reference position located 3° from the source position. Eight observations were conducted with an integration time of 3477 s each, and eight different local-oscillator (LO) tunings were used in order to allow deconvolution of the signal from the image side band. The LO tunings are shifted by 118 MHz up to 249 MHz. Inspection of the data shows no contamination from the reference position in any of the observations, nor from the image side-band. The total integration time is thus 7.7 h (27 816 s) for the on-off source integration.

The central frequency of the O₂ 3⁻₂ line is 487.249264 GHz with an upper level energy of E_u = 26.4 K and an Einstein A coefficient of 8.657 × 10⁻⁹ s⁻¹ (Drouin et al. 2010). In HIFI, two spectrometers are in operation, the “Wide Band Spectrometer” (WBS) and the “High Resolution Spectrometer” (HRS) with resolutions of 0.31 km s⁻¹ and 0.073 km s⁻¹ at 487 GHz, respectively. Owing to the higher noise ranging from a factor of 1.7 up to 4.7 of the HRS compared with the WBS, only WBS observations were used in the analysis. There is a slight difference between the pointings of the H and V polarizations in HIFI, but this difference of ΔHV (−6.2/ +2:2; Roelfsema et al. 2012) for Band 1 is small enough to be neglected relative to the beam size of 44″ (FWHM). Spectra from both polarizations were carefully checked for differences in intensities of other detected lines but none were found. Therefore the two polarizations were averaged to improve the signal to noise ratio.

Data processing started from the standard HIFI pipeline in the Herschel Interactive Processing Environment (HIPE) ver. 8.2.1 (Ott 2010), where the VLSR precision is of the order of a few m s⁻¹. The lines suffer from significant standing waves in each of the observations. Therefore a special task for HIFIFRINGE in HIPE was used to remove standing waves. The fitting routine was applied to each observation one by one and it successfully removed a large part of the standing waves. Further processing and analysis was done using the GILDAS-CLASS software. A first order polynomial was applied to all observations, which were subsequently averaged together. The standard antenna temperature scale T_A is corrected to the main beam temperature T_{MB} (Kutter & Ulrich 1981) by applying the efficiency of 0.76 for HIFI band 1a (Roelfsema et al. 2012, Fig. 2).

To understand and constrain the excitation and chemistry of O₂, complementary transitions in NO and C¹⁸O were observed. Nitrogen monoxide (NO) was observed with the James Clerk Maxwell Telescope (JCMT)³ using a beam size of 20″ as part of the M10BN05 observing program. The total integration time for this observation was 91 min. C¹⁸O J = 1–0 was observed with the IRAM 30 m telescope using a frequency-switch mode over an area of 1' x 1' in a 22″ beam. A C¹⁸O J = 3–2 spectrum was extracted from the large NGC 1333 map of Curtis et al. (2010), which was observed with the HARPB instrument at JCMT with position switch-mode (off position coordinate: 3₂⁻²⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻･⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻˓•›˓•‐˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’˓•’在传奇故事中，主角通过克服重重困难，最终实现了他的梦想。这不仅是一个关于勇气的故事，也是一个关于坚持和决心的故事。主角的旅程充满了挑战和危险，但他从未放弃过自己的梦想。最终，通过不懈的努力和坚持，他成功地实现了自己的目标。这个故事告诉我们，只要有决心和勇气，任何事情都是有可能实现的。
Fig. 2. Full spectrum taken with HIFI, with the H- and V-polarization spectra averaged. The frequency range is 483.59 GHz to 488.94 GHz from left to right. The entire bandwidth is 5.35 GHz. The O2 line is centred near $V_{\text{LSR}} = 7.0 \text{ km s}^{-1}$. A blow-up of the spectrum is presented in Fig. A.1.

Fig. 3. Spectrum of Fig. 2 magnified around the O2 $3_3-1_2$ line. The blue dashed line indicates the LSR velocity of the IRAS 4A envelope at 7.0 km s$^{-1}$ and the red dashed line shows the velocity at 8.0 km s$^{-1}$.

Fig. 4. Spectrum of the NO $J = 5/2-3/2$ transitions showing the location of four hyperfine (HF) components, where the details of the lines are given in Table 1. The spectrum is centred on the NO (3) (HF) component.

3. Results

In Fig. 2, the full Herschel-HIFI WBS spectrum is presented. Although the bandwidth of the WBS data is 4 GHz, the entire spectrum covers 5.35 GHz as a result of combining eight different observations where the LO frequencies were slightly shifted in each of the settings. The rms of this spectrum is 1.3 mK in 0.35 km s$^{-1}$ bin, therefore many faint lines are detected near the main targeted O2 $3_3-1_2$ line. These lines include some methanol (CH$_3$OH) lines, together with e.g., SO$_2$, NH$_2$D, and D$_2$CO lines. These lines are shown in Fig. A.1 in detail, and are tabulated with the observed information in Table A.1.

3.1. O$_2$

A blow-up of the HIFI spectrum centred around the O$_2$ $N_J = 3_3-1_2$ at 487 GHz position is presented in Fig. 3. The source velocity of IRAS 4A is $V_{\text{LSR}} = 7.0 \text{ km s}^{-1}$ as determined from many C$^{18}$O lines (Yıldız et al. 2012), and is indicated by the blue dashed line in the figure. This spectrum of 7.7 h integration time staring at the IRAS 4A source position is still not sufficient for a firm detection of the O$_2$ line at 487 GHz at the source velocity. However, a tentative detection at $V_{\text{LSR}} = 8.0 \text{ km s}^{-1}$ (red dashed line in Fig. 3) is seen and will be discussed in more detail in Sect. 5.

3.2. NO

In Fig. 4, the JCMT spectrum covering the hyperfine components of the NO $J = 5/2-3/2$ transitions are presented. For this specific transition, the expected ratios of the line intensities in the optically thin limit are NO (1):NO (2):NO (3):NO (4) = 75:126:200:24. The JCMT observations have an rms of 46 mK in 0.3 km s$^{-1}$ bin and 4σ emission is detected only at the intrinsically strongest hyperfine transition, NO (3), with an integrated intensity of 0.18 K km s$^{-1}$ centred at $V_{\text{LSR}} = 8.0 \text{ km s}^{-1}$. No emission is detected for the $V_{\text{LSR}} = 7.0 \text{ km s}^{-1}$ component, however 3σ upper limit values are provided in Table 2.
Table 2. Summary of the observed line intensities in a 44″ beam.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Transition</th>
<th>Telescope/Instrument</th>
<th>( \int T_{mb} dV ) [K km s(^{-1})]</th>
<th>( T_{peak} ) [K]</th>
<th>FWHM [km s(^{-1})]</th>
<th>( \int T_{mb} dV ) [K km s(^{-1})]</th>
<th>( T_{peak} ) [K]</th>
<th>FWHM [km s(^{-1})]</th>
<th>Rms [mK]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{O}_2 )</td>
<td>( N_J = 3_{3} - 1_{1} )</td>
<td>Herschel-HIFI</td>
<td>(&lt;0.0027) ( \ldots ) ( \ldots )</td>
<td>( 0.0069 )</td>
<td>1.3</td>
<td>( 8.0 ) ( \text{km s}^{-1} ) component(^a)</td>
<td>( 0.0046 )</td>
<td>1.3</td>
<td>1.3(^a)</td>
</tr>
<tr>
<td>( \text{C}^{18}\text{O} )</td>
<td>( J = 1 - 0 )</td>
<td>IRAM 30 m-EMIR</td>
<td>1.30</td>
<td>1.38</td>
<td>0.9</td>
<td>2.25</td>
<td>2.35</td>
<td>0.9</td>
<td>26(^a)</td>
</tr>
<tr>
<td>( \text{C}^{18}\text{O} )</td>
<td>( J = 3 - 2 )</td>
<td>JCMT-HARP-B</td>
<td>1.32</td>
<td>1.36</td>
<td>0.9</td>
<td>1.67</td>
<td>1.74</td>
<td>0.9</td>
<td>99(^a)</td>
</tr>
<tr>
<td>( \text{C}^{18}\text{O} )</td>
<td>( J = 5 - 4 )</td>
<td>Herschel-HIFI</td>
<td>0.39</td>
<td>0.36</td>
<td>1.0</td>
<td>0.13</td>
<td>0.13</td>
<td>1.0</td>
<td>10(^a)</td>
</tr>
<tr>
<td>NO (3)</td>
<td>( J = 5/2-3/2 ), ( F = 7/2-5/2 )</td>
<td>JCMT-RxA</td>
<td>(&lt;0.15) ( \ldots ) ( \ldots )</td>
<td>0.18</td>
<td>0.16</td>
<td>2.9</td>
<td>46(^a)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes. The values are calculated through a fit to the lines. \(^a\) \( V_{LSR} = 7.0 \) km s\(^{-1} \) component. \(^b\) \( V_{LSR} = 8.0 \) km s\(^{-1} \) component. \(^c\) 3\(\sigma\) upper limit. \( d\) In 0.35 km s\(^{-1} \) bins. \( e\) In 0.3 km s\(^{-1} \) bins.

Fig. 5. \( \text{O}_2 \) 3\(\rightarrow\)1\(_2\) spectrum overplotted with the \( \text{C}^{18}\text{O} \) 1–0, 3–2, and 5–4 lines in a 44″ beam. The \( \text{C}^{18}\text{O} \) spectra are scaled to the same peak intensity. Note the shift in velocity from 8.0 to 7.0 km s\(^{-1} \) with increasing \( J \).

3.3. \( \text{C}^{18}\text{O} \)

Figure 5 shows the \( \text{C}^{18}\text{O} \) 1–0, 3–2, and 5–4 lines overplotted on the \( \text{O}_2 \) line. The peak of the \( \text{C}^{18}\text{O} \) emission shifts from \( V_{LSR} = 8.0 \) km s\(^{-1} \) to 7.0 km s\(^{-1} \) as \( J \) increases. The \( \text{C}^{18}\text{O} \) 1–0 line is expected to come primarily from the surrounding cloud at 8.0 km s\(^{-1} \) due to the low energy of the transition (\( E_{up} = 5.3 \) K). On the other hand, the 5–4 line has higher energy (\( E_{up} = 79 \) K), therefore traces the warmer parts of the protostellar envelope at 7.0 km s\(^{-1} \). As a sanity check, the \( 13\text{CO} \) 1–0, 3–2, and 6–5 transitions from Yıldız et al. (2012) were also inspected and their profiles are consistent with those of the \( \text{C}^{18}\text{O} \) lines, however they are not included here due to their high opacities. The integrated intensities \( \int T_{mb} dV \) for each of the 7.0 km s\(^{-1} \) and 8.0 km s\(^{-1} \) components are given in Table 2.

3.4. Column densities and abundances

3.4.1. Constant excitation temperature results

A first simple estimate of the \( \text{O}_2 \) abundance limit in the IRAS 4A protostellar envelope (\( V_{LSR} = 7.0 \) km s\(^{-1} \) component) is obtained by computing column densities within the 44″ beam. The collisional rate coefficients for the \( \text{O}_2 \) 3\(\rightarrow\)1\(_2\) line give a critical density of \( n_{\text{cr}} = 1 \times 10^3 \) cm\(^{-3}\) for low temperatures (Lique 2010; Goldsmith et al. 2011). The density at the 5000 AU radius corresponding to this beam is found to be 4\( \times \)10\(^{15} \) cm\(^{-3}\) based on the spherical power-law density model of Kristensten et al. (2012, see also Fig. 6 and below). This value is well above the critical density, implying that the \( \text{O}_2 \) excitation is thermalized. High densities are independently confirmed by the detection of many high excitation lines from molecules with large dipole moments in this source (e.g., Jørgensen et al. 2005; Maret et al. 2005). The width of the \( \text{O}_2 \) 3\(\rightarrow\)1\(_2\) line is taken to be similar to that of \( \text{C}^{18}\text{O} \), \( \Delta V \approx 1.0 \) km s\(^{-1} \). The \( \text{O}_2 \) line is assumed to be optically thin and a temperature of 30 K is used. The 3\(\sigma\) \( \text{O}_2 \) column density limit at \( V_{LSR} = 7.0 \) km s\(^{-1} \) is then \( N(\text{O}_2) = 1.1 \times 10^{15} \) cm\(^{-2}\) assuming Eqs. (2) and (3) from Yıldız et al. (2012).

The total \( \text{H}_2 \) column density of the 7.0 km s\(^{-1} \) component in the 44″ beam is computed from the model of Kristensten et al. (2012) through \( N_{\text{H}_2,\text{beam}} = \int n_{\text{H}_2}(z, b) dG(b) 2\pi db \int G(b) 2\pi db \), where \( b \) is the impact parameter, and \( G(b) \) is the beam response function. The resulting value is \( N(\text{H}_2) = 2.1 \times 10^{23} \) cm\(^{-2}\), which is an order of magnitude lower than the pencil-beam \( \text{H}_2 \) column density of \( 1.9 \times 10^{24} \) cm\(^{-2}\). Using the 44″-averaged \( \text{H}_2 \) column density implies an abundance limit \( X(\text{O}_2) \leq 5.7 \times 10^{-9} \). This observation therefore provides the lowest limit on the \( \text{O}_2 \) abundance.
The above analysis assumes constant physical conditions along the line of sight as well as constant abundances. It is well known from multi-line observations of C\(^18\)O that the CO abundance varies throughout the envelope, dropping by more than an order of magnitude in the cold freeze-out zone (e.g., Jørgensen et al. 2002; Yıldız et al. 2010, 2012). A more sophisticated analysis of the O\(_2\) abundance is therefore obtained by using a model of the IRAS 4A envelope in which the density and temperature vary with position. The envelope structure presented in Fig. 6 has been determined by modeling the continuum emission (both the spectral energy distribution and the submillimeter spatial extent) using the 1D spherically symmetric dust radiative transfer code DUSTY (Ivezic & Elitzur 1997). A power-law density profile is assumed with an index \(n\), i.e., \(n = r^{-p}\), and the fitting method is described in Schöier et al. (2002) and Jørgensen et al. (2002, 2005), and is further discussed in Kristensen et al. (2012) with the caveats explained. The temperature is calculated as a function of position by solving for the dust radiative transfer through the assumed spherical envelopes, heated internally by the luminosity of the source. The gas temperature is assumed to be equal to the dust temperature. The envelope is defined from the inner radius of 33.5 AU up to the outer radius of 33,000 AU, where the density of the outer radius is \(1 \times 10^4\) cm\(^{-3}\). IRAS 4A is taken to be a standalone source; the possible overlap with IRAS 4B is ignored, but any material at large radii along the line of sight within the beam contributes in both the simulated and observed spectra.

The observed line intensities are used to constrain the molecular abundances in the envelope by assuming a trial abundance structure and computing the non-LTE excitation and line intensities with radiative transfer models for the given envelope structure. For this purpose, the Monte Carlo line radiative transfer program Ratran (Hoogerheide & van der Tak 2000) is employed. The simplest approach assumes a constant O\(_2\) abundance through the envelope. Figure 7 (left) shows different abundance profiles, whereas Fig. 8 (top left) shows the resulting line intensities overplotted on the observed O\(_2\) line. The light blue line in Figs. 7 and 8 is the maximum constant O\(_2\) abundance that can be hidden in the noise, which is \(2.5 \times 10^{-8}\). This is within a factor of 4 of the simple column density ratio estimate.

A more realistic abundance structure includes a freeze-out zone below 25 K where both O\(_2\) and CO are removed from the gas. Such a CO “drop” abundance profile has been determined for the IRAS 4A envelope via the optically thin C\(^18\)O lines from \(1-0\) to 10–9 in Yıldız et al. (2012). By using the best fit CO abundance structure and assuming a constant O\(_2\)/CO abundance ratio, an upper limit of O\(_2\)/C\(^18\)O \(\leq 1\) is obtained (see red line in Figs. 7 and 8), corresponding to O\(_2\)/CO \(\leq 2 \times 10^{-3}\).

With a 44″ beam, the 487 GHz line observed with HIFI is mostly sensitive to the bulk of the envelope. Nevertheless, the drop abundance models can be used to estimate the maximum O\(_2\) abundance on smaller scales, to get a firm observational constraint on how much O\(_2\) is in the region where it could enter the embedded circumstellar disk. The radius of such a disk is highly uncertain, but probably on the order of 100 AU (e.g. Visser et al. 2009). According to the drop abundance models, the maximum O\(_2\) abundance that can be “hidden” inside 100 AU is \(\sim 10^{-8}\). However, the full chemical models from Sect. 4 suggest the actual O\(_2\) abundance on these small scales is several orders of magnitude lower (Fig. 7, middle).

In summary, both the simple column density estimate and the more sophisticated envelope models imply a maximum O\(_2\) abundance of \(\sim 10^{-8}\), and an O\(_2\)/CO ratio of \(\lesssim 2 \times 10^{-7}\). For NO, the best fit drop abundance requires NO to be about 8 times lower in abundance than C\(^18\)O, to be consistent with our NO non-detection.

### 4. Gas-grain models for the protostellar envelope

The next step in the analysis is to compare the upper limit for the \(V_{\text{LSR}} = 7.0\) km s\(^{-1}\) component with full gas-grain chemical models. The Ohio State University (OSU) gas-grain network (Garrod et al. 2008) is used as the basis for the chemical network, which contains an extensive gas-grain chemistry. There are 590 gas phase and 247 grain surface species and 7500 reactions among

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**Table 3. Summary of column densities in a 44″ beam.**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Column density [cm(^{-2})]</th>
<th>Abundance w.r.t. H(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(N(7\text{ km s}^{-1}))</td>
<td>(N(8\text{ km s}^{-1}))</td>
</tr>
<tr>
<td>O(_2)</td>
<td>(1.2 \times 10^{15})</td>
<td>(2.8 \times 10^{15})</td>
</tr>
<tr>
<td>C(^18)O</td>
<td>(3.6 \times 10^{14})</td>
<td>(1.8 \times 10^{15})</td>
</tr>
<tr>
<td>NO</td>
<td>(1.9 \times 10^{14})</td>
<td>(2.3 \times 10^{14})</td>
</tr>
<tr>
<td>H(_2)</td>
<td>(2.1 \times 10^{23})</td>
<td>(1 \times 10^{22})</td>
</tr>
</tbody>
</table>

**Notes.** See text for the conditions used for the calculations. (a) \(\sigma\) column density limit. (b) Beam averaged H\(_2\) column density in a 44″ beam obtained from the model of Kristensen et al. (2012). (c) Computed using the average C\(^18\)O column density and abundance ratios of CO/H\(_2\) = \(10^{-4}\) and CO/C\(^18\)O = 550 (Wilson & Rood 1994).

---

observed to date. It is \(\sim 4\) orders of magnitude lower than the pure gas phase chemical model predictions of \(X(O_2) = 7 \times 10^{-9}\).

Another option is to compare the O\(_2\) column density directly with that of C\(^18\)O. These lines trace the part of the envelope where CO and, by inference, O\(_2\) are not frozen out because of their similar binding energies (Collings et al. 2004; Acharyya et al. 2007). Using the C\(^18\)O lines therefore provides an alternative constraint on the models. The C\(^18\)O lines are also thermalized, and assuming a temperature of 30 K, its inferred column density is calculated as \((3.2-6.1) \times 10^{15}\) cm\(^{-2}\), depending on the adopted lines. The corresponding abundance ratio is \(N(O_2)/N(C^{18}O) = 3.5\) so \(N(O_2)/N(CO) \leq 6.4 \times 10^{-3}\) assuming CO/C\(^18\)O = 550.

The critical densities for the NO transitions range from \(n_{c,(NO)} = 2.4 \times 10^7\) cm\(^{-3}\) to \(n_{c(NO)} = 7.0 \times 10^6\) cm\(^{-3}\), so LTE is again justified. For the \(3\sigma\) upper limit on the NO (3) line in the 7.0 km s\(^{-1}\) component, the inferred column density is \(N(NO) \leq 1.9 \times 10^{14}\) cm\(^{-2}\), assuming \(T_{\text{em}} = 30\) K and no beam dilution. Thus, the implied NO abundance is \(N(NO)/N(H_2) = X(NO) \leq 9.0 \times 10^{-10}\). All column densities and abundances associated with the protostellar source at \(V_{\text{LSR}} = 7.0\) km s\(^{-1}\) are summarized in Table 3.

### 3.4.2. Abundance variation models

The analysis assumes constant physical conditions along the line of sight as well as constant abundances. It is well known from multi-line observations of C\(^18\)O that the CO abundance varies throughout the envelope, dropping by more than an order of magnitude in the cold freeze-out zone (e.g., Jørgensen et al. 2002; Yıldız et al. 2010, 2012). A more sophisticated analysis of the O\(_2\) abundance is therefore obtained by using a model of the IRAS 4A envelope in which the density and temperature vary with position. The envelope structure presented in Fig. 6 has been determined by modeling the continuum emission (both the spectral energy distribution and the submillimeter spatial extent) using the 1D spherically symmetric dust radiative transfer code DUSTY (Ivezic & Elitzur 1997). A power-law density profile is assumed with an index \(p\), i.e., \(n \propto r^{-p}\), and the fitting method is described in Schöier et al. (2002) and Jørgensen et al. (2002, 2005), and is further discussed in Kristensen et al. (2012) with the caveats explained. The temperature is calculated as a function of position by solving for the dust radiative transfer through the assumed spherical envelopes, heated internally by the luminosity of the source. The gas temperature is assumed to be equal to the dust temperature. The envelope is defined from the inner radius of 33.5 AU up to the outer radius of 33,000 AU, where the density of the outer radius is \(1 \times 10^4\) cm\(^{-3}\). IRAS 4A is taken to be a standalone source; the possible overlap with IRAS 4B is ignored, but any material at large radii along the line of sight
Table 4. Rate coefficients for O₂ (Eq. (1)) and NO (Eq. (2)) formation.

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
<th>T [K]</th>
<th>Rate coeff. [cm³ s⁻¹]</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O₂</td>
<td>39–149</td>
<td>3.5 × 10⁻¹¹</td>
<td>Carty et al. (2006)</td>
</tr>
<tr>
<td>2</td>
<td>O₂</td>
<td>10</td>
<td>7.8 × 10⁻¹²</td>
<td>Lin et al. (2008)</td>
</tr>
<tr>
<td>3</td>
<td>O₂</td>
<td>10</td>
<td>5.4 × 10⁻¹³</td>
<td>Xu et al. (2007)</td>
</tr>
<tr>
<td>4</td>
<td>O₂</td>
<td>...</td>
<td>7.5 × 10⁻¹¹ × (T/300)^{-0.25}</td>
<td>OSU database</td>
</tr>
<tr>
<td>5</td>
<td>NO</td>
<td>...</td>
<td>7.5 × 10⁻¹¹ × (T/300)^{-0.18}</td>
<td>OSU database</td>
</tr>
</tbody>
</table>

Notes. (a) CRESU measurement; (b) without J-shifting; (c) with J-shifting.

them. The subsequent subsections discuss the various chemical processes chemical processes that were considered in the network and are relevant for O₂ and NO are discussed.

4.1. Gas phase O₂ and NO formation

In the gas, O₂ is predominantly formed via reaction (1) between O atoms and OH radicals. The rate coefficient of this reaction has been measured in the temperature range between 39 K and 142 K with the CRESU (Cinetique de Reaction en Ecoulement Supersonique Uniforme) technique by Carty et al. (2006) who found a rate coefficient of 3.5 × 10⁻¹¹ cm³ s⁻¹ that is constant with temperature. However, several theoretical calculations, especially below 39 K, also exist in the literature. Using quantum mechanical calculations with the so-called J-shifting approximation and neglecting non-adiabatic coupling, Xu et al. (2007) obtained a rate coefficient that decreases as the temperature drops from 100 to 10 K. At 10 K, the computed rate coefficient has fallen to a value of 5.4 × 10⁻¹³ cm³ s⁻¹, significantly lower than the 39 K experimental value. However, more recent calculations by Lin et al. (2008), in which the J-shifting approximation has been removed, find a rate coefficient at 10 K of 7.8 × 10⁻¹² cm³ s⁻¹, higher than the Xu et al. (2007) value but still only about 1/4.5 of the experimental value at 39 K. The O₂ formation rates are summarised in Table 4. We have used all three rate coefficients to compare the computed O₂ abundance with the measured upper limit.

Gas-phase NO is predominantly formed through reaction (2). Its gas-phase reaction rate coefficient is listed in Table 4. This reaction is taken from the OSU database and was first determined by Smith et al. (2004).

4.2. Grain chemistry specific to O₂ and NO

The grain surface chemistry formulation in the OSU code follows the general description by Hasegawa & Herbst (1993) for adsorption, diffusion, reaction, dissociation, and desorption processes, updated and extended by Garrod et al. (2008). The binding energies of various species to the surface are critical parameters in the model. In most of the models, we adopt the binding energies from Garrod & Herbst (2006) appropriate for a water-rich ice surface. However, the possibility of a CO-rich ice surface is also investigated by reducing the binding energies by factors of 0.75 and 0.5, respectively (Bergin et al. 1995; Bergin & Langer 1997).

The presence of O₂ on an interstellar grain can be attributed to two different processes. First, gas-phase O₂ can be accreted on the grain surface during the (pre-)collapse phase and second, atomic oxygen can recombine to form O₂ on the dust grain via the following reaction:

\[ \text{O} + \text{O} \rightarrow \text{O}_2. \]  

(3)

Following Tielens & Hagen (1982), 800 K is used as the binding (desorption) energy for atomic oxygen on water ice. The binding energy for O₂ on water ice is taken as 1000 K (Cuppen & Herbst 2007), which is an average value obtained from the temperature programmed desorption (TPD) data by Ayotte et al. (2001) and Collings et al. (2004). A ratio of 0.5 between the diffusion barrier...
and desorption energy has been assumed for the entire calculation (Cuppen & Herbst 2007), so the hopping energy for atomic oxygen is 400 K.

For this hopping energy, one oxygen atom requires $2 \times 10^3$ s to hop to another site at 10 K. For comparison, the time needed for a hydrogen atom to hop to another site is around 0.35 s, which is a factor of 10$^6$ faster. Therefore, instead of forming O$_2$, an accreted atomic oxygen species will be hydrogenated, leading to the formation of OH and H$_2$O. It is most unlikely that accreted atomic oxygen produces any significant amount of O$_2$ on the grain surface during the pre-collapse phase. Recent studies using the continuous time random walk (CTRW) Monte Carlo method do not produce significant O$_2$ on the grain surface (Cuppen & Herbst 2007). However, elevated grain temperatures ($\gtrsim$20 K), when the residence time of an H atom on the grain is very short and atomic oxygen has enhanced mobility, could be conducive to O$_2$ formation.

What happens to the O$_2$ that is formed in the gas phase and accreted onto the dust grains? There are two major destruction pathways. First, the reaction of O$_2$ with atomic H leads to the formation of HO$_2$ and H$_2$O$_2$, which then could be converted to water following reaction pathways suggested by Ioppolo et al. (2008) and Cuppen et al. (2010):

$$
\begin{align*}
O_2 & \overset{H}{\rightarrow} HO_2 \overset{H}{\rightarrow} H_2O_2 \overset{H}{\rightarrow} H_2O + OH. \\
\text{(4)}
\end{align*}
$$

Thus, a longer cold pre-collapse phase would significantly reduce O$_2$ on the dust grains and turn it into water ice, whereas a shorter pre-collapse phase would yield a higher solid O$_2$ abundance (Roberts & Herbst 2002). These reactions also depend on the grain temperature: at higher temperatures, the shorter residence time of H atoms on the grain leads to less conversion of O$_2$.

The second destruction route leads to the formation of ozone through

$$
O_2 + O \rightarrow O_3. \\
\text{(5)}
$$

This route is most effective at slightly higher grain temperatures ($\gtrsim$20 K) when atomic oxygen has sufficient mobility to find an O$_2$ molecule before it gets hydrogenated. Ozone could also be hydrogenated as suggested by Tielens & Hagen (1982) and confirmed in the laboratory by Mokrane et al. (2009) and Romanzin et al. (2010) leading back to O$_2$:

$$
\begin{align*}
O_3 & \overset{H}{\rightarrow} O_2 + OH. \\
\text{(6)}
\end{align*}
$$

Similarly, accreted NO on the grain surface can undergo various reactions. In particular, recent laboratory experiments have shown that NO is rapidly hydrogenated to NH$_2$OH at low ice temperatures (Congiu et al. 2012). A critical parameter here is the competition of the different channels for reaction of HNO + H$_2$, which can either go back to NO + H$_2$O or form H$_2$NO.

The final important ingredient of the gas-grain chemistry is the rate at which molecules are returned from the ice back into the gas phase. Both thermal and non-thermal desorption processes are considered. The first non-thermal process is reactive desorption; here the exothermicity of the reaction is channeled into the desorption of the product with an efficiency determined by a parameter $\epsilon_{\text{RRK}}$ (Garrod et al. 2007). In these model runs, a value of 0.01 is used, which roughly translates into an efficiency of 1%. Recently, Du et al. (2012) used 7% for the formation of H$_2$O$_2$.

Second, there is desorption initiated by UV absorption. Photodissociation of an ice molecule produces two atomic or radical products, which can subsequently recombine and desorb via the reactive desorption mechanism. The photons for this process derive both from the external radiation field and from UV photons generated by ionization of H$_2$ due to cosmic rays, followed by the excitation of H$_2$ by secondary electrons. The externally generated UV photons are very effective in diffuse and translucent clouds but their role in dense clouds is limited to the edge of the core (Ruffle & Herbst 2000; Hollenbach et al. 2009). The cosmic-ray-generated internal photons can play an effective role in the dense envelope, with a photon flux of $\approx 10^5$ photons cm$^{-2}$ s$^{-1}$ (Shen et al. 2004). We have considered both sources of radiation in our model. In either case, the rate coefficients for photodissociation on surfaces are assumed to be the same as in the gas phase.

Photodesorption can proceed both by the recombination mechanism described above as well as by kick-out of a neighboring molecule. The combined yields for a variety of species including CO and H$_2$O have been measured in the laboratory (Öberg et al. 2009a,b; Muñoz Caro et al. 2010) and computed through molecular dynamics simulations for the case of H$_2$O by Andersson & van Dishoeck (2008) and Arasa et al. (2010). Finally, there is the heating of grains via direct cosmic ray bombardment, which is effective for weakly bound species like CO and O$_2$ and included following the formulae and parameters of Hasegawa & Herbst (1993).

4.3. Model results

Our physical models have two stages, the “pre-collapse stage” and the “protostellar stage”. In the pre-collapse stage, the hydrogen density is $n_H = 10^7$ cm$^{-3}$, visual extinction $A_V = 10$ mag, the cosmic-ray ionization parameter, $\zeta = 1.3 \times 10^{-17}$ s$^{-1}$, and the (gas and grain) temperature, $T = 10$ K, which are standard parameters representative of cold cores. The initial elemental abundances of carbon, oxygen and nitrogen are $7.3 \times 10^{-5}$, $1.76 \times 10^{-4}$ and $2.14 \times 10^{-5}$, respectively, in the form of atomic C, O and N. All hydrogen is assumed to be in molecular form initially. In the second stage, the output abundance of the first phase is used as the initial abundance at each radial distance with the density, temperature and visual extinction parameters at each radius taken from the IRAS 4A model shown in Fig. 6. We assume that the transition to the protostellar phase from the pre-collapse stage is instantaneous, with the same ratio of mass, density and temperature structure are established quickly, consistent with evolutionary models (Lee et al. 2004; Young & Evans 2005).

To explain the observed spectra of O$_2$, both the pre-collapse time and protostellar time as well as the O$_2$ formation rates are varied. Analysis of CO and HCO$^+$ multi-line observations in pre and protostellar sources have shown that the high density pre-collapse stage typically lasts a few $10^5$ yr (e.g., Jørgensen et al. 2005; Ward-Thompson et al. 2007). The models $A$ to $Q$ have different parameters and timescales which are listed in Table 5. Those models result in abundance profiles in the envelope at each time step and radius. These profiles are then run in Ratran in order to compare directly with the observations.

Figure 7 (middle) shows examples of model abundance profiles. All model runs predict lower O$_2$ abundances than the evolutionary models of Visser et al. (2011), whose chemical network did not include any grain-surface processing of O$_2$. The line emission from our models is compared to the observations in Fig. 8 (bottom left). Table 5 summarizes the resulting O$_2$ peak temperatures for each of the models. All models except $H$ and $I$ overproduce the observed O$_2$ emission of at most a few mK, by up to two orders of magnitude in the peak temperature.
The models that are consistent with the data have in common longer pre-collapse stages; in particular Model J, which has the longest pre-collapse stage of 10^5 years, best fits the 3σ O2 limit. Using a lower rate coefficient for the O+OH reaction of 7.84 × 10^{-15} cm^3 s^{-1} (Lin et al. 2008) for the same best fit models (H_L and I_L) results in a factor of 5 lower emission. In this case, the pre-collapse stage can be shortened to ~7 × 10^5 yr (Model G_L).

For NO, the H and I models were calculated twice. In Case 1, hydrogenation of HNO leads back to NO and H₂ and in Case 2 hydrogenation of HNO leads to H₂NO as suggested by Congiu et al. (2012). Comparison of the results from Case 1 with observations shows significant overproduction of the observed NO emission, whereas Case 2 is consistent with an upper limit of 0.05 K (1σ). Therefore, a combination of both reactions appears to be needed.

These results for IRAS 4A suggest that a long pre-collapse stage is characteristic of the earliest stages of star formation, in which atomic and molecular oxygen are frozen-out onto the dust grains and converted into water ice, as proposed by Bergin et al. (2000). Similarly, the rapid conversion of NO to other species on the grains limits its gas-phase abundance. It is clear that the grain surface processes are much more important than those of the pure gas-phase chemistry in explaining the O₂ and NO observations. The timescale for NGC 1333 IRAS 4A is at the long end of that inferred more generally from observations.

The model results show that the fraction of O₂ in the gas and left on the grains must indeed be very small, dropping to ≤10^{-9} close to the protostar (Fig. 7, right). This in turn implies that the gas and ice that enter the disk are very poor in O₂. Although IRAS 4A is the only low-mass protostar that has been observed to this depth, the conclusions drawn for IRAS 4A probably hold more generally. Thus, unless there is significant production of O₂ in the disk, the icy planetesimals will also be poor in O₂.

### Table 5. Chemical models considered for the IRAS 4A protostellar envelope

<table>
<thead>
<tr>
<th>Model</th>
<th>Pre-collapse stage [yr]</th>
<th>Protostellar stage [yr]</th>
<th>O₂ formation rate [cm³ s⁻¹]</th>
<th>T_{peak}(O₂)[K]</th>
<th>T_{peak}(NO)[K]</th>
</tr>
</thead>
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<tr>
<td>A</td>
<td>5 × 10⁴</td>
<td>10³</td>
<td>7.5 × 10⁻¹ × (T/300)^⁻₀.₂₅</td>
<td>0.119</td>
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</tr>
<tr>
<td>B</td>
<td>1 × 10⁵</td>
<td>10³</td>
<td>7.5 × 10⁻¹ × (T/300)^⁻₀.₂₅</td>
<td>0.102</td>
<td>...</td>
</tr>
<tr>
<td>C</td>
<td>2 × 10³</td>
<td>10³</td>
<td>7.5 × 10⁻¹ × (T/300)^⁻₀.₂₅</td>
<td>0.085</td>
<td>...</td>
</tr>
<tr>
<td>D</td>
<td>3 × 10³</td>
<td>10³</td>
<td>7.5 × 10⁻¹ × (T/300)^⁻₀.₂₅</td>
<td>0.073</td>
<td>...</td>
</tr>
<tr>
<td>E</td>
<td>5 × 10³</td>
<td>10³</td>
<td>7.5 × 10⁻¹ × (T/300)^⁻₀.₂₅</td>
<td>0.042</td>
<td>...</td>
</tr>
<tr>
<td>F</td>
<td>6 × 10³</td>
<td>10³</td>
<td>7.5 × 10⁻¹ × (T/300)^⁻₀.₂₅</td>
<td>0.024</td>
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<tr>
<td>G₁₀</td>
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<td>10³</td>
<td>7.5 × 10⁻¹ × (T/300)^⁻₀.₂₅</td>
<td>0.011</td>
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</tr>
<tr>
<td>G₁₁</td>
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<td>10³</td>
<td>7.5 × 10⁻¹ × (T/300)^⁻₀.₂₅</td>
<td>0.0046</td>
<td>0.015</td>
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<tr>
<td>H₁₦</td>
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<td>10³</td>
<td>3.50 × 10⁻¹</td>
<td>0.0025</td>
<td>...</td>
</tr>
<tr>
<td>H₁₈</td>
<td>7 × 10³</td>
<td>10³</td>
<td>7.84 × 10⁻¹</td>
<td>0.0010</td>
<td>...</td>
</tr>
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</table>

#### Notes.
Models G, H, I, and J use different rate coefficients for O₂ formation (Eq. (1)), as indicated by subscripts: O for OSU, C for Carty et al. (2006), and L for Lin et al. (2008). (a) Ratran model results using a line width of 1.0 km s⁻¹. (b) Best fit models. For NO, Case 2 is tabulated.

#### 5. Tentative detection of O₂ in the 8 km s⁻¹ cloud

![Fig. 9. Tentative detection of the O₂ 3₃–1₂ line from the extended NGC 1333 cloud.](image)

Although there is no sign of O₂ emission at the velocity of the dense protostellar envelope (7.0 km s⁻¹), a 4.5σ tentative detection of O₂ 3₃–1₂ line emission is found at V_{LSR} = 8.0 km s⁻¹, the velocity of the more extended NGC 1333 molecular cloud (Fig. 9, Loren 1976; Lisèe et al. 1988). The feature is also seen in individual H and V polarization spectra. The peak intensity of the tentative detection is T_{mb} = 4.6 mK, the line width ΔV = 1.3 km s⁻¹, and the integrated intensity is ∫T_{mb} dV = 6.9 mK km s⁻¹ between the velocities of 6.5 to 9.7 km s⁻¹. The large HiFi beam size of 44″ encompasses both the extended cloud as well as the compact envelope. Since any O₂ emission is optically thin, the two components cannot block each other, even if slightly overlapping in velocity.
The density in the surrounding cloud at 8.0 km s$^{-1}$ is expected to be significantly lower than that in the envelope. Figure B.1 presents the $^{18}$O 3–2/1–0 ratio for the 8.0 km s$^{-1}$ component. The observed value is consistent with a wide range of kinetic temperatures from 20 K to 70 K, with corresponding densities in a narrow range from $7 \times 10^3$ to $2 \times 10^5$ cm$^{-3}$, respectively. $^{18}$O column densities from the 3–2 and 1–0 line intensities are then $(2.3\pm1.8) \times 10^{15}$ cm$^{-2}$ for this range of physical parameters.

For the same range of conditions, the O$_2$ column density is $(2.8\pm4.3) \times 10^{15}$ cm$^{-2}$ (Fig. 10). The inferred abundance ratios are $N$(O$_2$)/$N$(C$^{18}$O) = 1.2 to 2.4, and $N$(O$_2$)/$N$(CO) = $(2.2\pm4.3) \times 10^{-3}$. Assuming CO/H$_2$ = $4 \times 10^{-4}$ gives $N$(O$_2$)/$N$(H$_2$) = $(2.2\pm4.3) \times 10^{-7}$. Interestingly, the inferred O$_2$ abundance is in between the values found for the Orion and ρ Oph A clouds (Goldsmith et al. 2011; Liseau et al. 2012). By assuming $T_{kin} = 30$ K, the implied NO column density is $2.3 \times 10^{14}$ cm$^{-2}$, leading to $N$(NO)/$N$(O$_2$) = $(5.3\pm8.1) \times 10^{-3}$ and $N$(NO)/$N$(H$_2$) = $2.3 \times 10^{-8}$.

Can such an O$_2$ column density and abundance be reproduced by chemical models? For the surrounding cloud, a large gas-grain model is not needed. Instead, the PDR models of Hollenbach et al. (2009), which include a simplified gas-grain chemistry, are adequate to model the emission. Figure 11 is a plot adapted from Melnick et al. (2012), which shows the values of interstellar radiation field $G_0$ required to reproduce the range of O$_2$ column densities according to the model described in Hollenbach et al. (2009). The horizontal grey band bounds the total observed O$_2$ column density range of $(2.8\pm4.3) \times 10^{15}$ cm$^{-2}$, while the vertical green band shows the range of $G_0$ values required to produce this range of O$_2$ column densities for gas densities between $10^3$ cm$^{-3}$ and $10^7$ cm$^{-3}$. For our low inferred densities of $<10^3$ cm$^{-3}$, a high $G_0$ value of $300–650$ fits the data. There is no external source in the NGC 1333 region which can provide this level of UV illumination, not even the nearby B5 V type star BD+30$^{\circ}$549 ($\alpha = 3^h 29^m 19.7^s$, $\delta = +31^\circ 24^\prime 57^\prime 05$ (J2000); ~0.8 pc away; van Leeuwen 2007). The $G_0$ value from this star at our position is at most 2.8 and can therefore not explain the high-$G_0$ scenario. Models with a slightly higher (factor of 2) water ice photodesorption yield than the standard value of $Y_{\text{H}_2\text{O}} = 10^{-3}$ would fit better the low-$G_0$ regime, where the value of $G_0$ is between the interstellar value of 1 and 2.8. This value of $Y_{\text{H}_2\text{O}}$ is within the uncertainties of the laboratory (Öberg et al. 2009a) and theoretical work (Arasa et al. 2010). More generally, a factor of two uncertainty in abundance can readily result from the combined uncertainties of the individual rate coefficients that lead to O$_2$ formation and destruction (Wakelam et al. 2006), so it does not necessarily imply an increased value of $Y_{\text{H}_2\text{O}}$. Considering the uncertainties in rate coefficients as well as possible increase in $Y$, there does not seem to be a problem having the actual low value of $G_0$ produce the observed column density of molecular oxygen.

6. Conclusions

We have presented the first deep (7.7 h) Herschel-HIFI observations of the O$_2$ 3$_1$–1$_2$ line at 487 GHz towards a deeply embedded Class 0 protostar, NGC 1333 IRAS 4A. The results from the observations and models can be summarized as follows.

- No O$_2$ emission is detected from the protostellar envelope, down to a 3σ upper limit of X(O$_2$) $\leq 6 \times 10^{-9}$, the lowest O$_2$ abundance limit toward a protostar to date. The O$_2$/CO limit is $\leq 6 \times 10^{-3}$.

- A full gas-grain chemical model coupled with the physical structure of the envelope is compared to our data consisting of two stages, a “pre-collapse stage” and “protostellar stage”. Best fits to the observed upper limit on the O$_2$ line suggest a long pre-collapse stage (~$0.7–1 \times 10^6$ years), during which atomic oxygen is frozen out onto the dust grains and converted into water ice. Also, at least a fraction of NO must be converted to more complex nitrogen species in the ice.

- The low O$_2$ abundance in the gas and on the grains in the inner envelope implies that the material entering the disk is very poor in O$_2$. 

Fig. 10. Integrated intensities of O$_2$ are shown as contours for a range of model column densities as function of density (left) and temperature (right) for the 8.0 km s$^{-1}$ component. The yellow solid line is the observed integrated intensity of the tentative detection and the shaded region represents the range of column densities for their corresponding temperatures. Left: $T_{kin} = 30$ K is assumed for different densities and right: $n = 5 \times 10^3$ cm$^{-3}$ is assumed for different temperatures.

Fig. 11. Total O$_2$ column density as a function of $G_0$ and density (adapted from Melnick et al. 2012; Hollenbach et al. 2009) for the 8.0 km s$^{-1}$ component. The horizontal grey band shows the total O$_2$ column density range for the observed integrated intensity in the 8 km s$^{-1}$ component. The vertical green band presents the range of high-$G_0$ values required to produce this range of O$_2$ column densities for gas densities between $10^3$ cm$^{-3}$ and $10^7$ cm$^{-3}$, whereas the orange band presents the actual $G_0$. $Y_{\text{H}_2\text{O}}$ is the water ice photodesorption yield.
Cuppen, H. M., Ioppolo, S., Romanzin, C., & Linnartz, H. 2010, Phys. Chem. Curriculum, which is operated by the California Institute of Technology under contract with NASA. The authors are grateful to many funding agencies and the HIFI-ICC staff, who has been contributing for the construction of Herschel and HIFI for many years. HIFI has been designed and built by a consortium of institutes and university departments from across Europe, Canada and the United States under the leadership of SRON Netherlands Institute for Space Research, Groningen, The Netherlands and with major contributions from Germany, France and the US. Consortium members are: Canada: CSA, U.Waterloo; France: CESR, LAB, LERMA, IRAM; Germany: KOSMA, MPIfR, MPS; Italy: U.NI Maynooth; Australia: ASI, IFSI-INAF, Osservatorio Astronomico Nazionale (INAF); Netherlands: SRON, TUD; Poland: CAMK, CBK, Spain: Observatorio Astronómico Nacional (IGN), Centro de Astrobiología (CSIC-INTA). Sweden: Chalmers University of Technology – MC2, RSS & GARD; Ondasa Space Observatory; Swedish National Space Board, Stockholm University – Stockholm Observatory; Switzerland: ETH Zurich, FHNW; USA: Caltech, NASA/JPL, NHSC.

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References


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Appendix A: HIFI O₂ spectrum

Fig. A.1. Spectrum of Fig. 2 magnified over certain velocity ranges. In panel c) the O₂ 33–12 transition is shown. Identifications refer to the 7.0 km s\(^{-1}\) component.

Table A.1. Overview of the other lines observed in the same spectrum.

<table>
<thead>
<tr>
<th>Mol.</th>
<th>Trans.</th>
<th>(E_u/k_B) [K]</th>
<th>(A_{ul}) [s(^{-1})]</th>
<th>Frequency [GHz]</th>
<th>(\int T_{mb}dV) [mK km s(^{-1})]</th>
<th>(T_{peak}) [mK]</th>
<th>FWHM [km s(^{-1})]</th>
</tr>
</thead>
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<tr>
<td>NH₂D</td>
<td>2_0–1_0</td>
<td>47.2</td>
<td>(1.36 \times 10^{-4})</td>
<td>488.323810</td>
<td>25</td>
<td>10</td>
<td>3.4</td>
</tr>
<tr>
<td>H₂CS</td>
<td>14–13</td>
<td>188.8</td>
<td>(1.76 \times 10^{-3})</td>
<td>487.663321</td>
<td>28</td>
<td>9</td>
<td>3.3</td>
</tr>
<tr>
<td>H₁⁵CS</td>
<td>15–14</td>
<td>200.5</td>
<td>(1.77 \times 10^{-3})</td>
<td>487.615288</td>
<td>22</td>
<td>5</td>
<td>3.9</td>
</tr>
<tr>
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<td>143.3</td>
<td>(5.15 \times 10^{-4})</td>
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<td>80</td>
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<td>26.38</td>
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<td>...</td>
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<td>CH₃OH</td>
<td>4₃₃–4₄₄</td>
<td>60.9</td>
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<td>(1.00 \times 10^{-6})</td>
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<td>D₂CO</td>
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<td>280</td>
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<td>(4.90 \times 10^{-4})</td>
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<td>483.686308</td>
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</table>

Notes. The level energies, Einstein A coefficients, and line frequencies are from the LAMDA, JPL and CDMS databases (Schöier et al. 2005; Pickett et al. 2010; Müller et al. 2005). Rms is 1.3 mK and in 0.35 km s\(^{-1}\) bin. Identifications refer to the 7.0 km s\(^{-1}\) component.
Appendix B: RADEX calculations for C$^{18}$O

The integrated intensity ratio of C$^{18}$O 3–2/1–0 is equal to 0.74 for the 8.0 km s$^{-1}$ component. This ratio can be analysed using the RADEX non-LTE excitation and radiative transfer program (van der Tak et al. 2007) to constrain the physical parameters. Figure B.1 presents the integrated intensity ratios as function of temperature and density, obtained for optically thin conditions. The observed ratio is indicated in dash-dotted lines.

![Schematic cartoon showing the scenario of O2 emission originating from the surrounding cloud.](image)

**Fig. B.1.** Left: schematic cartoon showing the scenario of O2 emission originating from the surrounding cloud. Right: integrated intensity ratios calculated with RADEX, as function of temperature and density, for a C$^{18}$O column density of $5 \times 10^{14}$ cm$^{-2}$ (optically thin conditions). The C$^{18}$O 3–2/1–0 ratio is relevant for the surrounding NGC 1333 cloud, which is traced by the 8.0 km s$^{-1}$ component. Dash-dotted lines indicate the observed ratio of C$^{18}$O 3–2/1–0 = 0.74 for the $V_{\text{LSR}} = 8.0$ km s$^{-1}$ component.