

A SEARCH FOR O₂ IN CO-DEPLETED MOLECULAR CLOUD CORES WITH *HERSCHEL*EVA S. WIRSTRÖM¹, STEVEN B. CHARNLEY², MARTIN A. CORDINER^{2,3}, AND CECILIA CECCARELLI⁴¹ Department of Earth and Space Sciences, Chalmers University of Technology, Onsala Space Observatory, 439 92 Onsala, Sweden; eva.wirstrom@chalmers.se² Astrochemistry Laboratory, Mailstop 691, NASA Goddard Space Flight Center, 8800 Greenbelt Road, Greenbelt, MD 20770, USA³ Department of Physics, The Catholic University of America, Washington, DC 20064, USA⁴ Laboratoire d'Astrophysique, Observatoire de Grenoble, BP 53, F-38041 Grenoble cedex 09, France

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ABSTRACT

The general lack of molecular oxygen in molecular clouds is an outstanding problem in astrochemistry. Extensive searches with the *Submillimeter Astronomical Satellite*, *Odin*, and *Herschel* have only produced two detections; upper limits to the O₂ abundance in the remaining sources observed are about 1000 times lower than predicted by chemical models. Previous atomic oxygen observations and inferences from observations of other molecules indicated that high abundances of O atoms might be present in dense cores exhibiting large amounts of CO depletion. Theoretical arguments concerning the oxygen gas–grain interaction in cold dense cores suggested that, if O atoms could survive in the gas after most of the rest of the heavy molecular material has frozen out onto dust, then O₂ could be formed efficiently in the gas. Using *Herschel* HIFI, we searched a small sample of four depletion cores—L1544, L694-2, L429, and Oph D—for emission in the low excitation O₂ $N_J = 3_3-1_2$ line at 487.249 GHz. Molecular oxygen was not detected and we derive upper limits to its abundance in the range of $N(\text{O}_2)/N(\text{H}_2) \approx (0.6-1.6) \times 10^{-7}$. We discuss the absence of O₂ in the light of recent laboratory and observational studies.

Key words: astrochemistry – ISM: abundances – ISM: clouds – ISM: molecules – molecular processes

1. INTRODUCTION

Molecular oxygen has proven to be the most elusive molecule in the interstellar medium. Gas-phase chemical models predict that dense molecular gas (with hydrogen number densities $\sim 10^3-10^5 \text{ cm}^{-3}$) should contain large fractional abundances of O₂ ($\sim 10^{-6}-10^{-5}$) after $\sim 10^5$ years (e.g., Leung et al. 1984; Bergin et al. 2000). However, extensive searches in various astronomical environments by *Herschel*⁵, the *Submillimeter Astronomical Satellite* (SWAS), and *Odin* (with respective beam sizes of $<1'$, $4'$ and $9'$), have demonstrated that O₂ emission is extremely rare in molecular clouds. SWAS and *Odin* observations of molecular clouds constrained the O₂ abundance limits to lie in the range of $\approx (0.8-7) \times 10^{-7}$ (Goldsmith et al. 2000; Pagani et al. 2003). Tentative detections by SWAS (Goldsmith et al. 2002), and from ground-based observations of the ¹⁶O¹⁸O isotopologue (Pagani et al. 1993), both remain unconfirmed (Fuente et al. 1993; Marechal et al. 1997; Pagani et al. 2003). Upper limits on the abundance of solid O₂ tend to rule out the possibility that the missing O₂ is hidden in icy grain mantles (Vandenbussche et al. 1999).

The SWAS and *Odin* limits on O₂ abundance are several hundred times less than predicted in chemical models. *Herschel* observations have pushed these limits down even more, to lie in the range of $\approx (0.1-5) \times 10^{-8}$ for many sources (Goldsmith et al. 2011b). Thus far, O₂ has only been securely detected in Orion (Goldsmith et al. 2011a) and ρ Oph A (Larsson et al. 2007; Liseau et al. 2012).

Several theoretical explanations have been advanced to explain the low O₂ abundances (as summarized by Roberts & Herbst 2002), but calculations show that, most probably, the

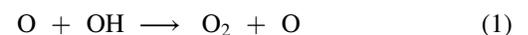
simple process of oxygen atom accretion and ice formation on cold dust grains is responsible (Bergin et al. 2000; Charnley et al. 2001; Viti et al. 2001; Roberts & Herbst 2002). These models show that, for cloud ages $\gtrsim 10^5$ years, once CO formation is complete, significant O atom depletion is necessary to prevent the O₂ abundance from violating the observed limits. However, it is generally unknown if the elemental abundance of oxygen in the observed molecular clouds is consistent with this explanation. Observations and theoretical models available at the time of the *Herschel* mission indicated that O atoms might be transiently much more abundant than CO (and C atoms) in some dense cores, and thus produce large abundances of O₂ in them. In this paper, we report the results of a *Herschel* HIFI search for O₂ in four cores that exhibit high degrees of CO depletion. Molecular oxygen was not detected and we provide upper limits.

2. OXYGEN IN DENSE MOLECULAR CLOUDS

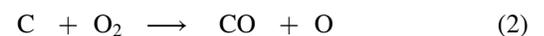
Our search for molecular oxygen was based on the state of observational and laboratory knowledge at the time of the *Herschel* mission.

2.1. Atomic Oxygen

Molecular oxygen is easy to form in both warm and cold dense gas through the neutral–neutral process



and is rapidly destroyed in the chemical reaction with atomic carbon



Once the conversion of atomic C to CO is almost complete ($\sim 10^5$ years), the O₂ abundance rises rapidly on a short timescale. Collisions of O atoms with cold dust, leading to the

⁵ *Herschel* is an ESA space observatory with science instruments provided by European-led Principal Investigator consortia and with important participation from NASA.

formation and retention of water ice, can occur on a comparable timescale and so inhibit interstellar O₂ production. However, there is no direct evidence for low atomic O abundances in cold clouds. In fact, large O/CO ratios have been measured in several sources, e.g., O/CO > 15 toward W49N (Vastel et al. 2000); where it has been attributed to selective CO depletion on grains; and O/CO ~ 50 toward L1689N (Caux et al. 1999). High fractional abundances of atomic O, $\approx 10^{-4}$, have also been measured in the collapsing envelope of the low-mass binary system IRAS 16293-2422 (Ceccarelli et al. 2000).

L1544 belongs to a family of cold starless cores in which CO molecules have been depleted from the gas (Bacmann et al. 2002; Bergin et al. 2002; Crapsi et al. 2005; Bergin & Tafalla 2007). Caselli et al. (2002) modeled the ionization of L1544, as determined from observations of HCO⁺, N₂H⁺, and their deuterated isotopologues, and concluded that a large fractional abundance of atomic O of $\approx 10^{-4}$ must be present to destroy H₃⁺ there, despite CO being significantly depleted onto dust. Gupta et al. (2009) detected C₆H⁻ and C₆H in the CO-depleted region of L1544. Subsequent modeling by Cordiner & Charnley (2012) determined that a similarly high gas-phase O atom abundance was required to destroy C₆H⁻ and thus account for the observed anion/neutral abundance ratio in this core, as well as in others that also show CO depletion (e.g., L1512). In L1544, and other dense cores, some carbon-bearing molecules (CN, HCN, HNC) are also present in the CO-depleted gas (Hily-Blant et al. 2010; Padovani et al. 2011) but at abundances much less than found in normal dark cloud gas, supporting the idea that C atoms are not particularly abundant in the gas.

In summary, there is some observational evidence that suggest oxygen atoms may not freeze out efficiently in some dense cores, even when CO and some other heavy molecules (e.g., CS) do. This, and the fact that the abundance of atomic C must also be significantly reduced, raises the possibility that CO-depleted cores could contain large abundances of O₂.

2.2. Gas-grain Chemistry of O₂

Could O₂ form in CO-depletion cores and be detectable? Here we demonstrate that this is theoretically possible. Models of O₂ suppression have simply assumed that gas-phase O atoms are hydrogenated to form H₂O ices (and thus removed) at the rates at which they collide and stick to grains (e.g., Bergin et al. 2000; Charnley et al. 2001; Viti et al. 2001; Roberts & Herbst 2002); experiments have confirmed the viability of this ice formation pathway (Dulieu et al. 2010). However, to maintain a population of O atoms in gas where CO is freezing out requires that collisions of oxygen atoms with cold grains do not result in 100% retention on the surface. Maret et al. (2006) have shown that the CO-depletion core B68 contains a significant abundance of N atoms as well as N₂ molecules and so it is reasonable to inquire whether this could also occur for O atoms.

Assumptions have been made in previous chemical models that could allow the return of O atoms to the gas at non-negligible rates (e.g., Hasegawa & Herbst 1993; Willacy & Williams 1993; Charnley et al. 2001; Viti et al. 2001; Caselli et al. 2002; Charnley & Rodgers 2002; Crapsi et al. 2005; Flower et al. 2005) and include: (1) lower than expected binding energies on the relevant surface, $E_0 = 600$ K,

(compare to 800 K, Tielens & Allamandola 1987), (2) a low sticking efficiency, (3) a variety of non-thermal desorption processes such as photodesorption or cosmic-ray impacts (Leger et al. 1985), or (4) desorption induced by H₂ formation (Willacy & Millar 1998). Thus, accepting that at least one of the above assumptions holds, it is feasible for an accreted O atom to desorb from a cold grain. However, since clearly some oxygen atoms must be retained on grains, the gas-grain kinetics of O atoms and CO molecules has to incorporate some degree of selective retention on the dust.

Hollenbach et al. (2009) have presented a model for photodissociation regions (PDRs), in which the O atoms can be thermally desorbed, and which treats water formation in a more kinetically realistic manner. On the grain surface, H atom addition first converts atomic O to OH, and these hydroxyl molecules can then form hydrogen bonds with pre-existing water molecules; if an O atom does not meet a surface H atom, there is a finite probability that it will desorb and return to the gas. The strengths of hydrogen bonds are typically at least a factor of 10 greater than those for van der Waals (physisorption) bonding, and it is this chemical fixing that controls the rate at which gaseous atomic O can become depleted on grains and suppress O₂ production. Thus, O atom accretion onto grains by fixing, as opposed to simply sticking at the gas-grain collision rate, depends on the gas-phase atomic O/H ratio, and is at its most efficient when the accreting gas has O/H < 1, and least so when oxygen atoms are more abundant than hydrogen atoms, i.e., when O/H > 1.

This naturally introduces a dependence on the density of the accreting gas. Because O atom removal explicitly depends on the H atom kinetics, water ice formation can occur easily at low densities ($\sim 10^4$ cm⁻³ or less) where O/H < 1 and the H/H₂ ratio has not yet reached a steady-state (corresponding to $n(\text{H}) \sim 1$ cm⁻³, Goldsmith & Li 2005). However, higher densities, $n(\text{H}_2) \sim 10^6$ cm⁻³, lead to an increased O/H ratio (>1) because H atoms are more efficiently converted to H₂ on grains, and consequently to less efficient O atom removal. CO freeze-out in cold cores (~ 5 – 10 K) becomes apparent at hydrogen densities in the range of $n(\text{H}_2) \sim 1.5 \times 10^4$ – 6×10^5 cm⁻³ (Jørgensen et al. 2005), and thus is concomitant with O/H > 1. Thus, counterintuitively, the central regions of dense cores exhibiting significant CO depletion may contain large abundances of O₂ ($\sim 10^{-6}$ – 10^{-5}).

An important point is that, at about 10 K, this O₂ will not react with H₃⁺ or any of its deuterated isotopologues, and thus would not affect the observed ionization or D/H enhancements found in these regions. The failure of previous searches for O₂ toward starless cores could then be attributed to not studying cores of sufficiently high CO depletion (L183 only has $f_D(\text{CO}) \sim 5$, Pagani et al. 2005), misalignment of the telescope beam with the depletion peak ($\sim 2'$ N of the TMC-2 position targeted by Fuente et al. 1993), beam dilution (SWAS and *Odin*, Goldsmith et al. 2000; Pagani et al. 2003), or some combination of the above.

One would expect that much of the H₂O formed from atomic oxygen will freeze out onto the dust; so, will O₂ suffer the same fate? N₂ freeze-out appears to set in at densities of $n(\text{H}_2) \sim 10^6$ cm⁻³ above that of CO (Belloche & André 2004; Pagani et al. 2005, 2012). The cause of his selective depletion in cold cores is poorly understood (Bergin & Tafalla 2007) but is unlikely to be connected to the difference in physisorption binding energies; these are measured to be very close:

Table 1
Source List with Observational Parameters

Source	R.A. (J2000.0) (^h ^m ^s)	decl. (J2000.0) ([°] ['] ["])	V_{LSR} (km s^{-1})	Obs Id
L429	18 17 05.1	-08 13 40	6.7	1342251645
Oph D	16 28 28.9	-24 19 19	3.5	1342250734
L1544	05 04 16.6	+25 10 48	7.2	1342250746
L694-2	19 41 04.5	+10 57 02	9.6	1342245385

855 ± 25 K for CO and 790 ± 25 K for N₂ (Öberg et al. 2005). Similarly, the measured O₂ binding energy of 912 ± 15 K (Acharyya et al. 2007) is sufficiently close to those of CO and N₂ that it is uncertain whether O₂ could exhibit selective depletion more like CO or N₂ at high densities. If the observed CO/N₂ depletion is connected to the fact that these homonuclear diatomic molecules are nonpolar (Masel 1996), then it might be expected that O₂ will persist after CO has become depleted, up to the density where N₂ is depleted, and perhaps beyond.

3. HERSCHEL OBSERVATIONS

In order to test whether O₂ abundances could be significantly enhanced in high-density depletion cores, we used the HIFI instrument (de Graauw et al. 2010) on board the *Herschel* Space Observatory (Pilbratt et al. 2010) to observe the $N_J = 3_3-1_2$ O₂ line at 487.249 GHz toward a sample of such sources, listed in Table 1. The sources were selected based on the known correlation between enhanced abundances of deuterated molecules and high CO depletion, and are the ones showing the highest CO-depletion factors, $f_D(\text{CO})$, in the surveys of H₂D⁺, N₂H⁺, and N₂D⁺ in starless cores by Crapsi et al. (2005) and Caselli et al. (2008). Observations targeted the N₂D⁺ emission peaks in the maps by Crapsi et al. (2005), which can be significantly offset from continuum core positions, but better tracing the depletion cores. Note that gas densities and temperatures in these cores are typically $n(\text{H}_2) > 10^5 \text{ cm}^{-3}$ and $T_K \sim 10$ K, which makes the 487.249 GHz line ($E_u = 26$ K) the most favorable one to observe in emission with HIFI, and collision rates fast enough for the fractional population of all energy levels to be well described by a Boltzmann distribution at the kinetic temperature.

The dual beam switching mode was employed with the LO frequency in HIFI band 1a set to 494.93 GHz in both L and R polarization, placing the line in the lower sideband. Both the Wide-Band Spectrometer (WBS) and the High Resolution Spectrometer (HRS) were used, and because emission lines from the region are known to be narrow (N₂D⁺ FWHM $\sim 0.2-0.4 \text{ km s}^{-1}$), the HRS was configured to high-resolution mode with a bandwidth of 230 MHz, corresponding to a spectral resolution of 125 kHz or $\sim 0.08 \text{ km s}^{-1}$ at this frequency. Observations were performed under observing program OT2_ewirst01_1 and the data presented here is available from the *Herschel* Science Archive⁶ (HSA) under observing IDs given in Table 1.

The beam FWHM is $44''$ at this frequency, the forward efficiency $\eta_1 = 96\%$, and the main-beam efficiency $\eta_{\text{mb}} = 76\%$. Detailed information about the HIFI calibration

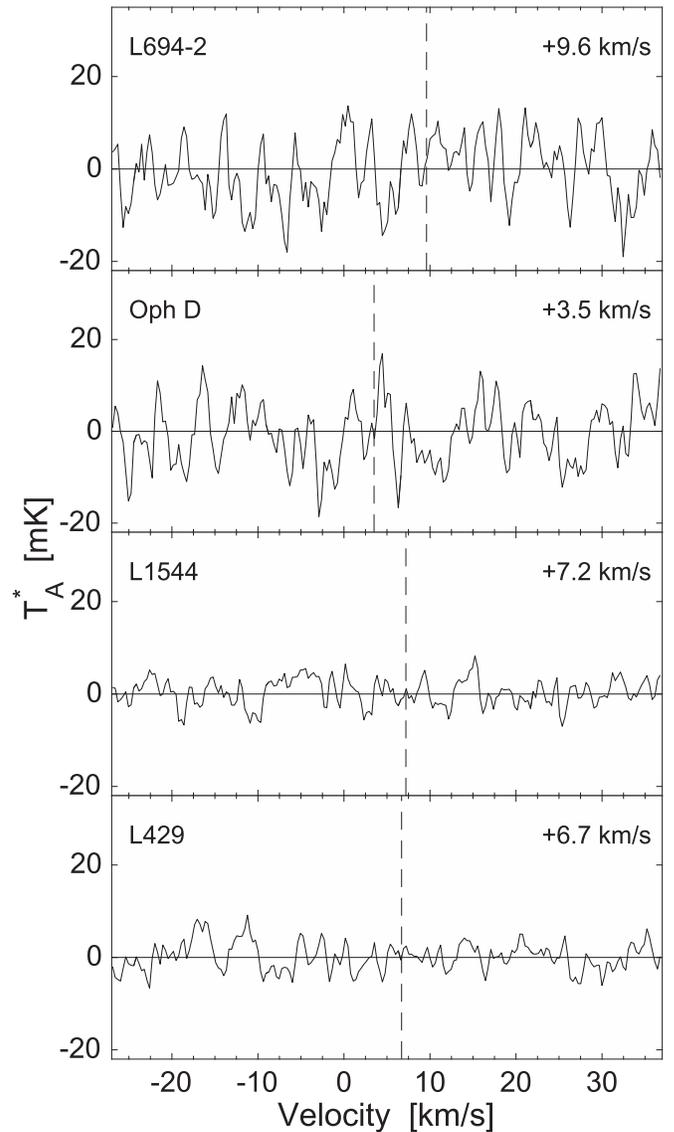


Figure 1. HIFI WBS spectra toward the four sources. The expected velocity of the O₂ 3₃-1₂ line, corresponding to the center velocity of N₂D⁺ emission (Crapsi et al. 2005), is given in the upper right corner of each spectrum and marked by vertical dashed lines to guide the eye.

including beam efficiency, mixer sideband ratio, pointing, etc., can be found on the *Herschel* website.⁷ The in-flight performance is described by Roelfsema et al. (2012).

Spectra of both polarizations were reduced separately using the *Herschel* Interactive Processing Environment (Ott 2010). Subsequently, data FITS files were exported to the spectral analysis software XS⁸ for further reduction and analysis. After linear baseline subtraction and frequency alignment, the two polarizations for each observing ID and spectrometer were averaged together, weighted by rms noise. Pointing offsets between polarizations were within $7''$, i.e., less than 20% of the beam size.

⁷ <http://herchel.esac.esa.int/>

⁸ Developed by Per Bergman at Onsala Space Observatory, Sweden; <http://www.chalmers.se/rss/oso-en/observations/data-reduction-software>.

⁶ <http://archives.esac.esa.int/hsa/aio/doc/>

Table 2
Adopted Source Parameters and Derived Oxygen Abundance Limits

Source	$n(\text{H}_2)^a$ cm^{-3}	T_{kin}^a K	$f_D(\text{CO})^a$	Δv^b km s^{-1}	$N(\text{H}_2)^a$ cm^{-2}	$N(\text{O}_2)^c$ cm^{-2}	$X(\text{O}_2)$	f_{dil}	$X_{\text{dil}}(\text{O}_2)^d$
L429	6e5	7	>20	0.4	1.2e23	<1.1e16	<9.2e-8	0.25	<1.2e-6
Oph D	5e5	7	~19	0.2	1.1e23	<1.2e16	<1.1e-7	0.32	<1.3e-6
L1544	2e6	7	~19	0.3	1.3e23	<8.2e15	<6.3e-8	0.17	<1.6e-6
L694-2	9e5	7	~16	0.3	1.1e23	<1.8e16	<1.6e-7	0.46	<1.3e-6

Notes.

^a From Caselli et al. (2008).

^b From N_2D^+ lines (Crapsi et al. 2005).

^c Beam averaged, 3σ upper limit.

^d Upper limit assuming the corresponding beam dilution factor f_{dil} ; see Section 4 for more details.

4. RESULTS AND ANALYSIS

Figure 1 shows the observed *Herschel* HIFI Wide-Band Spectrometer (WBS) polarization-averaged spectra toward the four sources in this study. Linear baselines have been subtracted and the resulting noise rms varies between 3 and 7 mK.

Molecular oxygen was not detected toward any of the cores. Before further analysis, spectra were multiplied by the total efficiency factor of $\eta_1/\eta_{\text{mb}} = 1.27$ (HIFI Observers' Manual version 2.4) in order to get them on the T_{mb} scale. For estimates of the O_2 abundance upper limits, the non-LTE radiative transfer code RADEX was used to model the level populations of O_2 molecules and 3σ line intensity upper limits. The spectroscopic data was adapted from Drouin et al. (2010) and collision rates with H_2 scaled from $\text{He} + \text{O}_2$ collision rates of Lique (2010). Physical conditions of the cores, listed in Table 2, were adapted from Caselli et al. (2008), while line widths were taken to be the same as for N_2D^+ . Table 2 presents the beam averaged upper limits on O_2 column densities based on these calculations, and upper abundance limits to O_2/H_2 in the range of $\approx(0.6-1.6) \times 10^{-7}$, assuming a constant H_2 column density over an area larger than the beam.

If the O_2 gas is only present in the inner, most CO-depleted parts of the cores, the emission would be significantly diluted in the large HIFI beam, and higher abundances could remain undetected. For example, assuming Gaussian O_2 source distributions with half intensities close to the 90% contours of the N_2D^+ maps by Crapsi et al. (2005), the abundance limits are instead of the order of 10^{-6} , see Table 2 for corresponding beam dilution factors and abundances.

5. DISCUSSION

Recent experiments indicate a much higher physisorption binding energy for O atoms on amorphous water ice (1660 ± 60 K; He et al. 2015). This is almost twice the value previously considered in chemical models (800 K, Tielens & Allamandola 1987) and was in fact suggested by Hollenbach et al. (2009). Model calculations confirm that, in the case of PDRs, higher O atom sticking efficiencies lead to a significant reduction in the gas-phase O_2 abundance (He et al. 2015). Nevertheless, the low O_2 abundances inferred in CO-depletion cores can only be explained by these models if the gas-phase atomic oxygen abundance is significantly lower than 10^{-5} .

The inferred low abundance of atomic oxygen in L1544 is consistent with the low gaseous H_2O abundance measured by Caselli et al. (2012) since higher O atom abundances would also produce more water (e.g., Bergin et al. 2000). On the other hand, it is too low to be consistent with the O atom abundances of $\leq 10^{-4}$ required to explain the anion/neutral ratios in the same source (Cordiner & Charnley 2012). Experiments show that O atoms could diffuse on grain surfaces faster than by pure thermal hopping (Minissale et al. 2014), so when $\text{O}/\text{H} > 1$ in the accreting gas, reactions between O atoms (Tielens & Hagen 1982) could form solid O_2 efficiently (see Charnley 2005), though some may be hydrogenated to H_2O (Ioppolo et al. 2008; Oba et al. 2009). Photodesorption of this O_2 would be dissociative (Fayolle et al. 2013) and would not increase the O_2 abundance in the gas of, say, L1544. Also, O_2 is predicted to have a higher physisorption binding energy to amorphous water ice when considering a low fractional coverage (1310 K; He et al. 2016) compared to previous experimental estimates considering monolayer coverage (Acharyya et al. 2007). This effect is even larger for CO and N_2 , resulting in an O_2 sticking efficiency that is significantly lower than that of CO, and following more closely that of N_2 (He et al. 2016). However, competition for binding sites between these O_2 molecules and CO molecules arriving on the surface could lead to their ejection into the gas (Noble et al. 2015). Our O_2 non-detections could therefore place limits on these processes in CO-depleted cores.

We did not detect molecular oxygen at abundances as high as 10^{-6} in the survey of depletion cores. The derived upper limits of $\sim 10^{-7}$ or less are similar to those obtained elsewhere. Yıldız et al. (2013) determined $\text{O}_2/\text{H}_2 \leq 6 \times 10^{-9}$ in NGC 1333 IRAS 4A, though there is a tentative O_2 detection in the surrounding cloud material. A low value for O_2/H_2 of 5×10^{-8} has been detected in ρ Oph A by Liseau et al. (2012). The widespread distribution of D-enriched formaldehyde and the detection of H_2O_2 in ρ Oph A (Bergman et al. 2011a, 2011b) both support the idea that the O_2 could be present following the evaporation of ice mantles from dust grains. A search for H_2O_2 in Orion was unsuccessful (Liseau & Larsson 2015), though the upper limits for hydrogen peroxide in interstellar ices, $\text{H}_2\text{O}_2/\text{H}_2\text{O} < 9\%$, do not rule out the possibility of it being quite abundant on dust grains (Smith et al. 2011). In Orion, the O_2 emission is confined to the H₂ Peak 1 position and the originally reported abundance ratio was $\text{O}_2/\text{H}_2 \sim 10^{-6}$ (Goldsmith et al. 2011b). A combination of postshock chemistry in a UV-illuminated MHD shock wave

with a fortuitous line of sight can account for the presence of O₂ in Orion, and suggest that the O₂ abundance could possibly be even higher $\sim 10^{-5}$ – 10^{-4} (Chen et al. 2014; Melnick & Kaufman 2015). In Sgr A, Sandqvist & Larsson (2015) find $O_2/H_2 \leq 5 \times 10^{-8}$ but also suggest that higher abundances, $O_2/H_2 \leq 1\text{--}2 \times 10^{-5}$, could exist in foreground clouds.

In conclusion, as with much of the dense interstellar medium, O₂ is underabundant in CO-depletion cores, most probably due to a large degree of O atom freezeout to form water ice. The reasons why it remains so generally underabundant and yet is detectable in a few sources remains a mystery, and there is little prospect of detection in additional sources in the near future with *Herschel* concluded and no follow-up space-based spectrometer in the pipeline. Nevertheless, understanding the interstellar O₂ deficiency can shed light on many poorly understood issues in astrochemistry (Melnick et al. 2012).

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Facility: *Herschel*(HIFI).

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