We present Herschel/HIFI observations of the fundamental rotational transitions of ortho- and para-\(^{16}\)O and \(^{18}\)O in absorption towards Sagittarius B2(M) and W31C. The ortho/para ratio in water in the foreground clouds on the line of sight towards these bright continuum sources is generally consistent with the statistical high-temperature ratio of 3, within the observational uncertainties. However, somewhat unexpectedly, we derive a low ortho/para ratio of \(\sim 2.35 \pm 0.35\), corresponding to a spin temperature of \(\sim 27\) K, towards Sagittarius B2(M) at velocities of the expanding molecular ring. Water molecules in this region appear to have formed with, or relaxed to, an ortho/para ratio close to the value corresponding to the local temperature of the gas and dust.

**Key words.** astrochemistry – ISM: abundances – ISM: molecules – molecular processes – submillimeter: ISM

## 1. Introduction

Water molecules play an essential role in the physics and chemistry of the dense interstellar medium (ISM). Water is one of the main reservoirs of oxygen, and as an important coolant of dense gas it strongly affects its star formation properties. For a molecule with two hydrogen atoms, such as water, the ortho/para ratio is temperature dependent and, in principle, the temperature of the medium in which the proton spin state populations last equilibrated can be deduced from the observations. Water is an asymmetric top molecule, with energy levels labeled by the set of quantum numbers \(J, K_{-1}, K_{+1}\), where \(K_{-1}, K_{+1}\) are the limiting prolate and oblate symmetric top quantum numbers. Levels with \(K_{-1} + K_{+1}\) even are para, and those with \(K_{-1} + K_{+1}\) odd are ortho. There are no fast radiative transitions between the two species of water, ortho and para. However, a collision resulting in a proton exchange, with a proton or \(H^+\) ion, can cause an ortho-para conversion in a water molecule. Such conversion can also result from interaction between a water molecule and the grain surface on which it is adsorbed. The lowest ortho state of water is 34.2 K above the para ground state. The ortho/para ratio in water is 3 in the high temperature limit. Departures from this limiting value are seen for nuclear spin temperatures below \(\sim 50\) K, with the ratio dropping to 1.5 at \(\sim 18\) K (see Fig. 4 of Mumma et al. 1987).

The ground-state rotational transition of \(o\)-water at 557 GHz was studied extensively in the ISM by the SWAS and Odin satellites (Melnick & Bergin 2005; Hjalmarson 2004). However, the HIFI instrument (de Graauw 2010) aboard the Herschel Space Observatory (Pilbratt et al. 2010) allows for the first time high-precision measurements of the fundamental p-water line at 1113 GHz. Measurements of the ortho/para ratio in water, by means of absorption spectroscopy in cold foreground clouds on sightlines towards bright submillimeter continuum sources, can provide key insights into the thermal history of the gas. The ortho/para ratio in water has been measured in several solar system comets and the derived nuclear spin temperatures are typically of order 30 K (see Crovisier et al. 1997; Kawakita et al. 2004).

## 2. Observations

HIFI observations of the ortho and para \(^{16}\)O and \(^{18}\)O towards Sagittarius B2(M) and W31C presented here were carried out between 2010 March 1 and March 5, using the dual beam switch (DBS) observing mode, as part of guaranteed time
The source coordinates are: $\alpha_{J2000} = 17^h47^m20.35^s$ and $\delta_{J2000} = -28^\circ23'03.0''$ for Sagittarius B2(M) and $\alpha_{J2000} = 18^h10^m28.7^s$ and $\delta_{J2000} = -19^\circ55'50.0''$ for W31C. The DBS reference beams lie approximately 3' east and west (i.e. perpendicular to the roughly north–south elongation of Sagittarius B2). We used the HIFI wide band spectrometer (WBS) providing a spectral resolution of 1.1 MHz (~0.6 km s$^{-1}$) at 557 GHz) over a 4 GHz IF bandwidth. The spectra presented here are equally-weighted averages of the H and V polarizations, reduced using HIPE (Ott 2010) with pipeline version 2.6. The resulting Level 2 double sideband (DSB) spectra were exported to the FITS format for a subsequent data reduction and analysis using the IRAM GILDAS package.

The band 1a, 1b and 4b spectral scans of Sagittarius B2(M) consist of DSB spectra with a redundancy of 8, which gives observations of a specific lower or upper sideband frequency with 8 different settings of the local oscillator (LO). This observing mode allows for the deconvolution and isolation of a single sideband (SSB) spectrum (Comito & Schilke 2002). We applied the standard deconvolution routine within CLASS. The observations of water lines in W31C were obtained using the DBS single standard deconvolution routine within CLASS. The observations in both H162O and H182O spectra divided by the background emission, including dust continuum and the SO2 lines. The o-H182O lines are saturated over a wide range of velocities and thus unusable for a quantitative analysis. However, we have identified several velocity ranges with moderate saturation levels, marked with thick horizontal lines in Fig. 2. These can be identified with the expanding molecular ring (< ~50 km s$^{-1}$), a transition between the 4 kpc arm and the Orion arm (~12 to ~7 km s$^{-1}$), the Sagittarius arm (5 to 20 km s$^{-1}$), and the Scutum arm (27 to 35 km s$^{-1}$, possibly blended with the Sagittarius B2 envelope; see e.g. Neufeld et al. 2000). Assuming that the foreground absorption completely covers the continuum and all water molecules are in the ground state (a reasonable assumption for the diffuse foreground clouds given the very high spontaneous emission rate coefficients for the ground-state water lines, $3.458 \times 10^{-3}$ and $1.842 \times 10^{-2}$ s$^{-1}$ for the ortho and para lines, respectively), we derive optical depths of the o- and p-water lines ($\tau = -\ln I/I_0$). The resulting optical depth ratio is shown in Fig. 2 (lower panel; left intensity scale). An ortho/para optical depth ratio of 1 corresponds to a column density ratio of 2. The resulting ortho/para
Fig. 2. (Upper) Spectra of the ground state o- and p-H\(_{18}\)O lines towards Sagittarius B2(M) normalized by the continuum (green and red histograms, respectively). (Middle) Corresponding spectra of the H\(_{16}\)O lines. (Lower) The ortho/para optical depth ratio (left scale) and column density ratio (right scale) as a function of LSR velocity. Black and blue lines, respectively Sagittarius B2 normalized by the continuum (green and red histograms, respectively).

Fig. 3. (Upper) Spectra of the ground state o- and p-H\(_{18}\)O lines towards W31C normalized by the continuum (green and red histograms, respectively). (Lower) The ortho/para optical depth ratio (left scale) and column density ratio (right scale) as a function of LSR velocity.

Table 1. Column densities (cm\(^{-2}\)) and ortho/para ratios towards Sagittarius B2(M).

| V (km s\(^{-1}\)) | O/P | N(H\(_{16}\)O) | N(H\(_{18}\)O) | X(H\(_{18}\)O) |
|-------------------|-----|----------------|----------------|--------------|
| −135 to −110      | 2.35 ± 0.3 | 3.0 × 10\(^{14}\) | 3.7 × 10\(^{14}\) | 6 × 10\(^{-7}\) |
| −73 to −52        | 2.35 ± 0.4 | 3.7 × 10\(^{14}\) | 6 × 10\(^{20}\) | 6 × 10\(^{-7}\) |
| −12 to −7         | 2.8 ± 0.5  | 1.2 × 10\(^{14}\) | 4 × 10\(^{20}\) | 3 × 10\(^{-7}\) |
| 5 to 20           | 3.0 ± 0.6  | 6.7 × 10\(^{15}\) | 3 × 10\(^{21}\) | 2 × 10\(^{-6}\) |
| 27 to 35          | 2.3 ± 0.3  | 1.7 × 10\(^{14}\) | 6 × 10\(^{20}\) | 3 × 10\(^{-7}\) |

The ortho/para ratio in the two velocity ranges between −12 and 20 km s\(^{-1}\) is consistent with the high-temperature limit of 3, within the uncertainties. The ratio in the Scutum arm, at 27 to 35 km s\(^{-1}\) is lower than 3. However, this component may be blended with the Sagittarius B2 envelope. The low ortho/para ratios derived at the envelope velocities, from both H\(_{16}\)O and H\(_{18}\)O data, are likely caused by the excitation effects. Given the higher density of the gas, the assumption that all water molecules are in the ground state is no longer correct. The column density of o-H\(_{2}\)O is more strongly affected, resulting in a lower apparent ortho/para ratio. In fact, we do see wings of the p-H\(_{18}\)O line in emission at the envelope velocities (Fig. 2; middle panel). Deriving the ortho/para ratio in water in the Sagittarius B2 envelope requires detailed radiative transfer modelling and is beyond the scope of the present Letter.

We derive a low ortho/para ratio, 2.35 ± 0.35, at velocities <−50 km s\(^{-1}\), corresponding to the expanding molecular ring. In this case, the measurement uncertainties are small enough that the ortho/para ratio of 3 appears to be ruled out by our data.

The o- and p-water spectra towards W31C, normalized by the continuum, are shown in Fig. 2 (upper panel). Weak p-H\(_{18}\)O absorption is seen at the cloud systemic velocity, but no o- or p-water optical depths have been added in quadrature.

Table 1 gives weighted averages of the ortho/para column density ratio in different velocity ranges towards Sagittarius B2(M), along with the corresponding uncertainties. Since the individual measurements are not independent but dominated by instrumental systematics, we use a more conservative estimate of the uncertainty of the mean for the two velocity intervals corresponding to the expanding molecular ring, computed from the peak-peak variation between the individual data points. The H\(_2\)O (ortho+para) column densities are also included, assuming an H\(_{16}\)O/H\(_{18}\)O ratio of 500 for the 5–20 km s\(^{-1}\) component. We compute H\(_2\)O column densities in the foreground gas using the method employed in Lis et al. (2001), based on O\(_2\)CO absorption data, assuming a CO abundance of 1 × 10\(^{-4}\) and a O\(_2\)CO/H\(_{18}\)O ratio of 60 in the local gas in the Sagittarius arm (5–20 km s\(^{-1}\) velocity range) and 30 in the remaining velocity intervals. The resulting column densities should be accurate to within a factor of 2. The H\(_2\)O abundance in the various components is generally consistent with that derived by Neufeld et al. (2000; 4–7 × 10\(^{-5}\)). The derived H\(_2\)O abundance in the 5–20 km s\(^{-1}\) component, based on the H\(_{18}\)O measurements, is a factor of 3–6 higher than that derived for the other components based on the H\(_{16}\)O data. However, the H\(_{18}\)O optical depth in this velocity range is low leading to large uncertainties. The water column density and abundance in this velocity range would be a factor of 2 lower if the gas responsible for the absorption is located in the envelope (Fig. 2; middle panel).

Fig. 2. (Upper) Spectra of the ground state o- and p-H\(_{18}\)O lines towards Sagittarius B2(M) normalized by the continuum (green and red histograms, respectively). (Middle) Corresponding spectra of the H\(_{16}\)O lines. (Lower) The ortho/para optical depth ratio (left scale) and column density ratio (right scale) as a function of LSR velocity. Black and blue points correspond to the H\(_2\)O and H\(_2\)O measurements, respectively.
\( \text{p-H}_{2}^{18}\text{O} \) absorption is detected in the foreground clouds. Once again, we have identified 3 velocity ranges where the \( \text{p-H}_{2}^{18}\text{O} \) lines are not completely saturated (thick horizontal lines in Fig. 2, upper panel). The resulting ortho/para ratio is relatively uniform, 2.8 ± 0.2, consistent with the high-temperature ratio of 3 within the measurement uncertainty (Fig. 2, lower panel).

4. Discussion

In the high-temperature limit one might expect an ortho/para ratio close to 3, when water is first formed. In the gas-phase, the excess energy of the exothermic reactions (e.g., recombination of \( \text{H}_{2}\text{O}^{+} \)) could lead to spin equilibration. For water molecules desorbed from ices on grain surfaces, one might also expect the initial ortho/para ratio to be 3 if there is enough energy to desorb a water molecule, either thermally or non-thermally, there is likely enough energy to populate numerous rotational states of the gas-phase species, both ortho and para, preserving a ratio close to 3 independent of the ortho/para ratio in the ice. However, the excess energy of formation is shared with the surface and the water ortho/para ratio may rapidly equilibrate at the grain temperature (e.g., Limbach et al. 2006).

Once water molecules are in the gas phase, collisions with atomic and molecular ions (\( \text{H}^{+} \) and \( \text{H}_{2}^{+} \)) can lead to proton exchanges and, over time, produce a gas-phase ortho/para ratio below 3 and potentially commensurate with the gas temperature (see the discussion of \( \text{H}_{2} \) conversion by Flower et al. 2006). As the temperature approaches zero, all water molecules will be in the ground para state if collisions with ions can efficiently exchange the ortho and para states. If there are no ions present, and therefore no barrierless collisions to exchange the ortho and para states of water, the ortho/para ratio of 3 will remain, independent of the temperature. Since ions are present in the ISM, we can expect the water ortho/para ratio to be generally lower than 3, given sufficient time. The time scale of the ortho/para conversion depends on the gas density. In dense clouds, there is a greater likelihood that the ortho/para ratio equilibrates at the gas kinetic temperature, as long as the density of ions is sufficient. In warmer, diffuse clouds, equilibrium would favor higher ortho/para ratios, but at lower densities equilibrium is less likely. Assuming a gas density of \( 10^{6} \text{ cm}^{-3} \), a fractional abundance of protonated ions of \( 10^{-5} \), and a rate coefficient of \( 10^{-16} \text{ cm}^{3} \text{ s}^{-1} \), we estimate the time scale of the ortho-para equilibration to be of order 3 \( \times 10^{3} \) years.

We derive a low ortho/para ratio of 2.35 ± 0.35, corresponding to a spin temperature of \( \sim 27 \text{ K} \), towards Sagittarius B2(M) at velocities corresponding to the expanding molecular ring. The low ortho/para ratio may suggest water formation on dust grains, with water molecule spin populations equilibrated at the dust temperature. Alternatively, the high-temperature ratio of 3 may have relaxed in the gas-phase to a value in line with the kinetic temperature of these clouds – a gas/dust temperature of order 30 K is quite reasonable for these relatively diffuse clouds within \( \sim 200 \text{ pc} \) from the Galactic center (e.g., Tiefentrunk et al. 1994). The water ortho/para ratio has now been measured in atmospheres of 9 solar system comets. The derived spin temperatures range between 23 and 34 K, with an average of \( \sim 29 \text{ K} \) (Crovisier, priv. comm.), close to our measurement in the expanding molecular ring.

The higher ortho/para ratio, consistent with the statistical ratio of 3, that we derive towards Sagittarius B2(M) in the velocity range \( -12 \) to \( 20 \text{ km s}^{-1} \) may indicate higher gas or dust temperatures (e.g., Gardner et al. 1988). Schilke et al. (2010) also derive a higher \( \text{H}_{2}\text{O}^{+} \) spin temperature towards this source at positive velocities, as compared to the line-of-sight clouds at negative velocities. In addition, strong chlorine absorption has been detected towards Sagittarius B2(S) at velocities between \( -10 \) and \( 20 \text{ km s}^{-1} \) (Lis et al. 2010). Since the \( \text{H}_{2}\text{Cl}^{+} \) abundance is enhanced in warm, UV-irradiated regions, this indicates the presence of a warm, diffuse gas component in this velocity range.

In summary, in the diffuse regions studied here, both water formation mechanisms (gas and solid state) can contribute. With sufficient time (or higher densities with subsequently faster gas-phase reactions) chemistry in the gas can drive the spin temperature towards the gas temperature. In addition, it has been postulated (Hollenbach et al. 2009) that photodesorption of water ices in low-density environments can release frozen molecules with a spin temperature that could agree with that of the dust grains. If the gas and dust temperatures are not equal this can lead to a ratio that reflects a mixture of these effects. Modeling the ortho/para ratio evolution is beyond the scope of this Letter, but the theme is that a ratio below 3 reflects cold environments (gas or dust temperatures below about 50 K).

With improved calibration and better understanding of the instrumental effects, more accurate determination of the water ortho/para ratio in these and other sources will be possible in the future. However, the present work clearly demonstrates the outstanding spectroscopic capabilities of HIFI for providing robust constraints for the physical conditions and chemistry of the ISM.

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