# Ortho/Para Ratio of H_2O^+ Toward Sagittarius B2(M) Revisited

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ABSTRACT: The HIFI instrument aboard the *Herschel* satellite has allowed the observation and characterization of light hydrides, the building blocks of interstellar chemistry. In this article, we revisit the ortho/para ratio for H_2O^+ toward the Sgr B2(M) cloud core. The line of sight toward this star forming region passes through several spiral arms and the gas in the Bar potential in the inner Galaxy. In contrast to earlier findings, which used fewer lines to constrain the ratio, we find a ratio of 3, which is uniformly consistent with high-temperature formation of the species. In view of the reactivity of this ion, this matches the expectations.
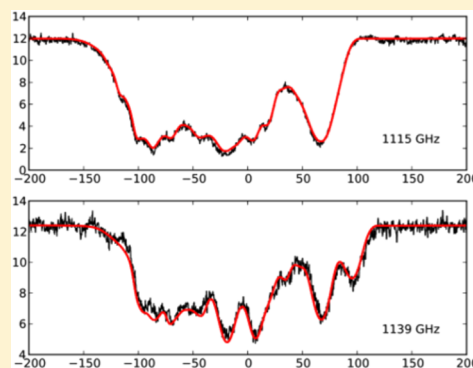
INTRODUCTION

The HIFI heterodyne instrument[1] on the *Herschel* satellite[2] provided the opportunity, for the first time, to observe and characterize hydrides, the fundamental building blocks of interstellar chemistry with high spectral resolution. This was previously not possible, with a few exceptions (OH, H_2S, SH^+, and OH^+)[3,4] because these relatively light molecules have their fundamental transitions at frequencies that are blocked by atmospheric water lines. These observations allow to determine the relative abundances and therefore test the chemistry. A particularly rewarding source is the high-mass star forming region Sgr B2(M), situated close to the Galactic center, because the line of sight toward this very bright far-infrared source passes through spiral arms and through much of the gas in the inner Galaxy.[5−7]

The data also permit determining the ortho/para ratio for a number of species (H_2O[8,9] and NH_3[10]). This had been done too for H_2O^+ by Schilke et al.,[11] with the surprising result that the ratio was found to be extremely low (about unity) in the 30−50 km s^{-1} range, which corresponds to the Scutum arm in the Galactic disk, while it was almost constant at 4.8 in the rest of the velocity range, which comprises very diverse environments. Since the ortho-state is the lower state, the high-temperature limit of the ortho/para ratio is the ratio of the nuclear spin weights, 3. At lower spin temperatures, there would be less *para*-H_2O^+, and the ratio would be higher. One therefore would not expect a ratio lower than 3. A ratio of unity could also occur if the formation happens at high temperatures, but no rotational excitation is involved,[12] which is unlikely to happen in one cloud only. However, already in this article the possibility of a measurement error due to contamination by

lines from unrelated molecules was mentioned. This possibility existed since *ortho*-H_2O^+ was observed in only one line, while *para*-H_2O^+, for which four lines were observed, showed strong blending with emission lines from the background source, at the low frequencies of these transitions, between 604 and 634 GHz. At these frequencies, emission lines from the Sgr B2(M) core are still strong, while they are strongly attenuated by dust at THz wavelengths.

The Schilke et al.[11] article was written before the full HEXOS (Herschel Key Project, Herschel/HIFI Observations of EXtraOrdinary Sources: The Orion and Sagittarius B2 Starforming Regions) full-band line survey of Sgr B2(M) was available. Now that one more *ortho*-H_2O^+ and three more *para*-H_2O^+ lines, at THz frequencies, have been observed, it seems appropriate to revisit the column density determination, which is the topic of the current article.

OBSERVATIONS

Full spectral scans of HIFI bands 1 to 7 toward Sgr B2(M) ($\alpha_{J2000} = 17^h47^m20.35^s$ and $\delta_{J2000} = -28°23'03.0''$) have been carried out in Dual Beam Switch (DBS) mode, with the DBS reference beams used to subtract instrumental and atmospheric noise located approximately 3′ east and west. The Wide Band Spectrometer (WBS) has been used as a back-end, providing a

spectral resolution of 1.1 MHz over a 4-GHz-wide Intermediate Frequency (IF) band. A HIFI Spectral Scan consists of a number of double-sideband (DSB) spectra, tuned to different Local Oscillator (LO) frequencies, where the spacing between one LO setting and the next is determined by the "redundancy" chosen by the observer.[13]

The data have been calibrated through the standard pipeline released with version 6 of HIPE,[14] and subsequently exported to CLASS, distributed with the GILDAS software[15] using the HiClass task within HIPE. Deconvolution of the DSB data into single-sideband (SSB) format has been performed in CLASS. All the HIFI data presented here, spectral features *and* continuum emission, are deconvolved SSB spectra. The intensity scale is the main-beam brightness temperature and results from applying beam efficiency corrections.[16] The HEB band 6b, which contains the 1.6 THz *para*-H_2O^+ lines, was recalibrated using HIPE 9, which offers sensitivity improvements for the HEB bands.

■ RESULTS AND DISCUSSION

The data fitting was done in the software package CASA,[17] using a port of the XCLASS program,[18,19] in conjunction with MAGIX.[20] The line profile, with its many velocity components, was fitted with Gaussian components, assuming an excitation temperature of 2.7 K, the cosmic background temperature. This is the excitation temperature any molecule will assume in the low density limit, which we believe to be the case here. In the Galactic center, the far-infrared background will contribute to the radiation field, but this will not significantly change the results. The fitting takes optical depth into account, but there is no unique solution for the number of components since there is significant velocity overlap. Using the spectra directly to determine the column density per velocity channel, in the manner done for water[9] is not possible, at least not for *ortho*-H_2O^+ since the lines have hyperfine structure. This procedure can be thought of as deconvolving the observed spectrum with the hyperfine pattern. Since the lines are generally optically thin, this procedure is robust against the number of components used, i.e., the recovered column density distribution should be independent of the details of the Gaussian components used to fit the absorption. The spectral line data used come from CDMS[21,22] (see also Table 1). Any uncertainty in derived line frequencies would result in a relative shift of the determined column densities and thus the ortho/para ratio. Depending on the individual errors on the lines, these could be washed out since always multiple lines were fitted. We do not

see any strong signature of a systematic shift between *ortho*-H_2O^+ and *para*-H_2O^+.

For *ortho*-H_2O^+, the results agree with Schilke et al.,[11] apart from a scaling factor (Figure 1). This shows that the *ortho*-
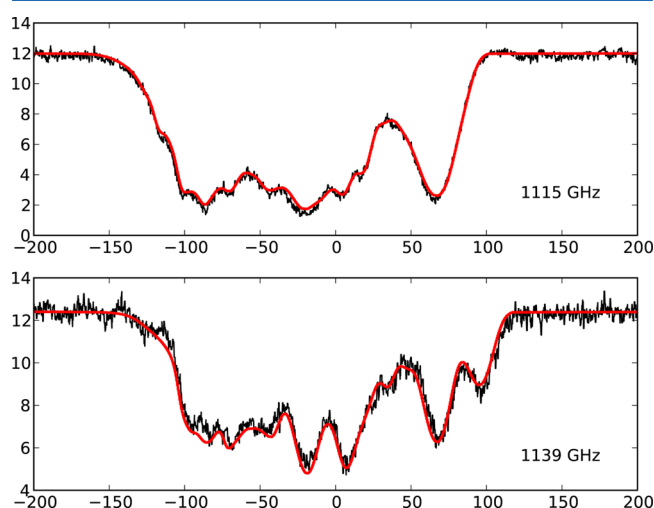

Figure 1. Spectra of *ortho*-H_2O^+ toward Sgr B2(M), with the fit shown in red.

H_2O^+ line was not contaminated by emission or absorption lines. The scaling comes from an incorrect estimation of the partition function at 2.7 K in Schilke et al.[11] In the fit, the partition function is extrapolated from the CDMS database value at 9.75 K and has to be corrected, which was not done properly in the earlier study. The partition functions used for *ortho*-H_2O^+ and *para*-H_2O^+ at 2.7 K were 5.9960 and 5.9125, respectively.

Three *para*-H_2O^+ lines were used in the fit: the relatively uncontaminated line at 607 GHz, and the lines at 1626 and 1638 GHz, which do show absorption. A good fit could be found (Figure 2), which is also compatible with the lines not used in the fit. A small discrepancy exists for the 64 km s^{-1} component, which corresponds to the Sgr B2 envelope component, and most likely is not well represented with an excitation temperature of 2.7 K. This component has to be modeled differently, taking the excitation conditions into account, and will not be considered further in this article, which concentrates on the diffuse line-of-sight components.

The ortho/para ratios turn out to be almost constant, 3.2 ± 0.4, with the values going significantly below 3 at about 50 km s^{-1} (Figure 3). The value there is less reliable than for other velocity ranges since it is in the wing of the 64 km s^{-1} envelope absorption and therefore affected by the above-mentioned uncertainties in the excitation, as well as blending with $H^{13}CO^+(7-6)$ at 607 GHz. However, even there the ratio of 3 is within the uncertainties, which are based on a 20% error in the column density estimation for each species.[16] The reported deviation from a constant ratio in the 30–50 km s^{-1} range[11] therefore was, as suspected, an artifact due to emission line contamination of the *para*-H_2O^+ lines.

Thus, the results presented here are consistent with a uniform ortho/para ratio of 3, which is the high temperature limit. Neufeld et al.[23] have shown, based on the OH^+/H_2O^+ ratio, that H_2O^+ is resident in gas, which is mostly atomic with only a small molecular fraction, generally a few percent. This is also true along the line of sight toward Sgr B2(M) (Schilke et

Table 1. List of Observed Transitions, Taken from CDMS[21,22]

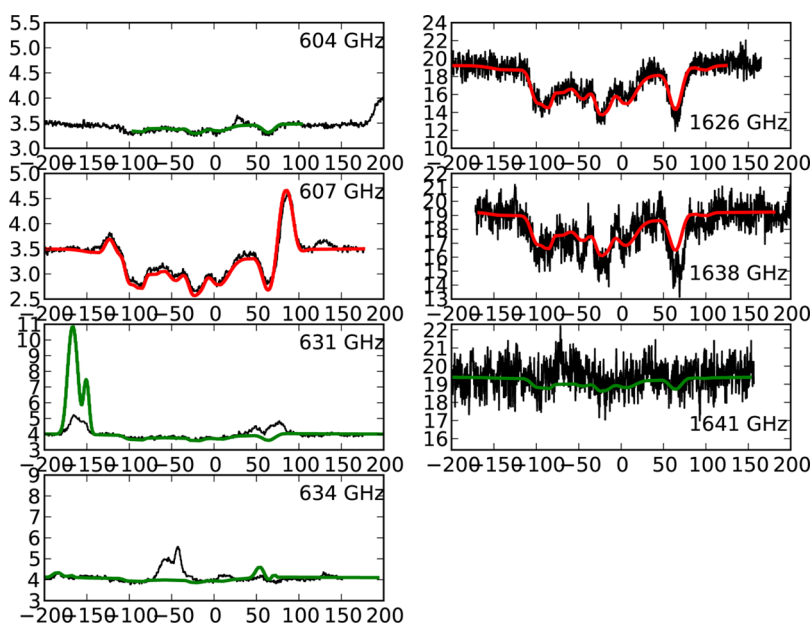| species	transition	frequency [GHz]	(f)it/(n)o fit
ortho-H_2O^+	$1_{1,1}, J = 3/2 - 0_{0,0}, J = 1/2$	1115.2	f
	$1_{1,1}, J = 1/2 - 0_{0,0}, J = 1/2$	1139.7	f
para-H_2O^+	$1_{0,0}, J = 3/2 - 1_{0,0}, J = 1/2$	604.7	n
	$1_{0,0}, J = 3/2 - 1_{0,0}, J = 3/2$	607.2	f
	$1_{0,0}, J = 1/2 - 1_{0,0}, J = 1/2$	631.7	n
	$1_{0,0}, J = 1/2 - 1_{0,0}, J = 3/2$	634.3	n
	$2_{1,2}, J = 5/2 - 1_{0,1}, J = 3/2$	1626.3	f
	$2_{1,2}, J = 3/2 - 1_{0,1}, J = 1/2$	1638.9	f
	$2_{1,2}, J = 3/2 - 1_{0,1}, J = 3/2$	1641.5	n

Figure 2. Spectra of *para*-H$_2$O$^+$ toward Sgr B2(M), with the fit. For the lines that were actually fitted, the fit is plotted in red; the other lines, which were not used in the fit (because of contamination or very low S/N ratio) are shown in green.
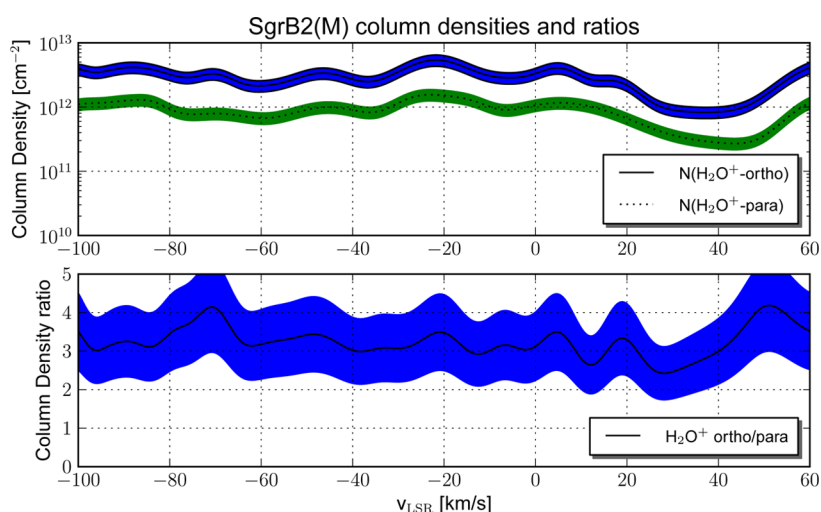

Figure 3. Column densities and column density ratios of *ortho*-H$_2$O$^+$/*para*-H$_2$O$^+$.

al., in preparation). A more detailed discussion of the chemistry of oxygen hydrides is found in Hollenbach et al.[24] This environment ensures that H$_2$O$^+$ is constantly formed by the highly exothermic (1.2 eV) reaction OH$^+$ + H$_2$ → H$_2$O$^+$ + H, and destroyed by dissociative recombination or, to a lesser degree, through H$_2$O$^+$ + H$_2$ → H$_3$O$^+$ + H. The energy difference between *ortho*-H$_2$O$^+$ and *para*-H$_2$O$^+$ is 30.1 K (or 0.2% of the energy available in the reaction), so from these energetic considerations it seems reasonable to expect that the molecule is formed with an abundance ratio of 3, the ratio of the nuclear spin weights. It is not obvious, however, that this argument is valid for H$_2$O$^+$. Herbst and Roueff[12] show that, because of the short lifetime of H$_2$O$^+$, the ortho/para ratio of H$_2$ involved in formation of H$_2$O$^+$ is imprinted in the ortho/para ratio of H$_2$O$^+$. Herbst and Roueff conclude that an ortho/para ratio of 3, as observed here, is most likely if the long-range hopping of a hydrogen atom is the mechanism of forming H$_2$O$^+$ from OH$^+$ and H$_2$. Other reactions also could play a role: ortho-to-para conversion could happen through *para*-H$_2$O$^+$ +

H$_2$, H → *ortho*-H$_2$O$^+$ + H$_2$, H, although it is unknown what fraction of the reaction with H2 goes into a proton exchange and which fraction would produce H$_3$O$^+$, and it is equally unknown if the proton exchange reaction with H happens at all. In contrast to H$_2$O, H$_2$O$^+$ is such a short-lived molecule that the ortho/para ratio will have no time to thermalize before the molecule is destroyed. Overall, it seems likely that the pristine ortho/para ratio will not change, and the observations are consistent with this expectation.

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Notes

The authors declare no competing financial interest.

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