

DISCOVERY OF INTERSTELLAR HEAVY WATER

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ABSTRACT

We report the discovery of doubly deuterated water (D_2O , heavy water) in the interstellar medium. Using the James Clerk Maxwell Telescope and the Caltech Submillimeter Observatory 10 m telescope, we detected the $1_{10}-1_{01}$ transition of para- D_2O at 316.7998 GHz in both absorption and emission toward the protostellar binary system IRAS 16293–2422. Assuming that the D_2O exists primarily in the warm regions where water ices have been evaporated (i.e., in a “hot corino” environment), we determine a total column density of $N(D_2O)$ of $1.0 \times 10^{13} \text{ cm}^{-2}$ and a fractional abundance of $D_2O/H_2 = 1.7 \times 10^{-10}$. The derived column density ratios for IRAS 16293–2422 are $D_2O/HDO = 1.7 \times 10^{-3}$ and $D_2O/H_2O = 5 \times 10^{-5}$ for the hot corino gas. Steady state models of water ice formation, either in the gas phase or on grains, predict D_2O/HDO ratios that are about 4 times larger than that derived from our observations. For water formation on grain surfaces to be a viable explanation, a larger H_2O abundance than that measured in IRAS 16293–2422 is required. Alternatively, the observed D_2O/HDO ratio could be indicative of gas-phase water chemistry prior to a chemical steady state being attained, such as would have occurred during the formation of this source. Future observations with the *Herschel Space Observatory* satellite will be important for settling this issue.

Subject headings: astrochemistry — ISM: individual (IRAS 16293–2422) — ISM: molecules — stars: formation

1. INTRODUCTION

It has long been known that the cold temperatures found in dense molecular clouds (~ 10 – 30 K) would be conducive to the selective incorporation of deuterium atoms into interstellar molecules (see Watson 1976 and references therein). At 10 K, the zero-point energy difference between H_2D^+ and H_3^+ leads to the former ion becoming sufficiently abundant that large numbers of D atoms can be distributed to other molecules through ion-molecule exchange reactions (e.g., Millar et al. 1989). The abundance of deuterated molecules can be significantly enhanced (to a few percent of the common variant), compared to the much smaller Galactic D/H ratio ($\sim 1.5 \times 10^{-5}$). The main reservoir is HD, but electron dissociative recombination of H_2D^+ leads to enhanced concentrations of free D atoms in the gas. Catalytic reactions on dust grains, driven by the accretion of H and D atoms from the gas, can therefore also produce large D enrichments in interstellar ices (Tielens 1983; Charnley et al. 1997). Deuterium enrichments are found in meteorites and comets, and so interstellar deuteration may have a connection with that of primitive solar system matter (e.g., Nuth et al. 2006).

Over the last few years, observations have found very high D/H ratios in some molecules, $\sim 10,000$ times the Galactic value (for reviews, see Ceccarelli 2002; Roueff & Gerin 2003; Ceccarelli et al. 2007), as well as doubly deuterated and triply deuterated isotopologues of common interstellar molecules, such as

ammonia, hydrogen sulfide, thioformaldehyde, formaldehyde, and methanol (Lis et al. 2002; van der Tak et al. 2002; Vastel et al. 2003, 2004; Marcelino et al. 2005; Parise et al. 2002, 2004). The region containing the low-mass protostellar binary system IRAS 16293–2422 has been particularly well studied in deuterated molecules (van Dishoeck et al. 1995; Ceccarelli et al. 2007). In IRAS 16293–2422, it appears that several of the deuterated molecules (e.g., water and methanol; Parise et al. 2002, 2005) are present in small “hot corinos,” the low-mass analogs of the hot molecular cores found in regions of massive star formation, in which icy grain mantles have been evaporated (Cazaux et al. 2003; Kuan et al. 2004; Bottinelli et al. 2004). The origin of this “superdeuteration” lies in gas-grain chemical processes associated with cold prestellar cores. In these dense regions ($\geq 10^6 \text{ cm}^{-3}$), as CO molecules are lost from the gas through condensation onto dust (e.g., Bacmann et al. 2003), the abundances of H_2D^+ , HD_2^+ , D_3^+ , and atomic D all increase dramatically and drive the fractionation chemistry to produce greatly elevated molecular D/H ratios (Roberts et al. 2003).

Comparison of the HDO/H_2O ratios of comets with that of ocean water and with interstellar ratios can provide important cosmogonic information (Meier et al. 1998; Bockelée-Morvan et al. 1998). In moving toward a complete understanding of interstellar deuterium chemistry, the detection of several key isotopologues will be required. An important, yet puzzling, aspect of interstellar deuteration concerns the markedly low levels of deuterium fractionation commonly measured in water, especially when compared to other molecules. The lower HDO/H_2O ratios ($\sim 3 \times 10^{-4}$) measured in massive hot molecular cores (e.g., Jacq et al. 1990; Gensheimer et al. 1996) are consistent with ion-molecule chemistry at around 30 K (Millar et al. 1989), whereas the highest ratios (0.004–0.01) are more suggestive of grain-surface reactions (Pardo et al. 2001). Recently, it has become possible to compare solar system D/H ratios with those of more primitive analog systems. In the protostellar binary system IRAS 16293–2422, the bounds on the measured range of HDO/H_2O ratios (2×10^{-4} to 3×10^{-2} ; Stark et al. 2004; Parise

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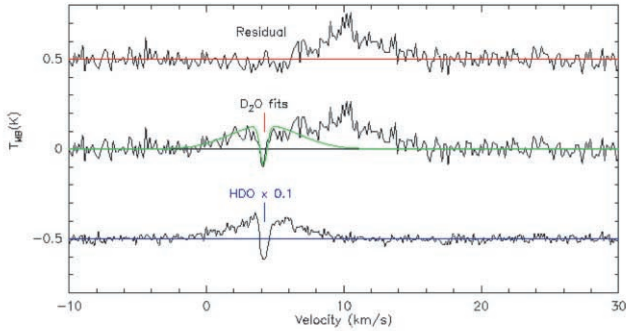


FIG. 1.—The $1_{10}-1_{01}$ transition of para- D_2O at 316.7998 GHz detected in emission and in absorption toward I16293A (center). A two-Gaussian component fit (green), using the velocity width and V_{LSR} of the HDO line reported by Stark et al. (2004), is superimposed on the D_2O spectrum. This HDO line (scaled by $\times 0.1$) is shown at bottom and, on top, an emission component is evident in the residual spectra obtained after the D_2O Gaussians have been subtracted.

et al. 2005) are determined by the abundances measured in the cold extended envelope and in the hot corino. Furthermore, Ceccarelli et al. (2005) have detected HDO in the DM Tau protoplanetary disk and have argued that photodesorption of water ices could lead to $HDO/H_2O \geq 0.01$ in the outer disk gas (Ceccarelli & Dominik 2005).

Interstellar water could be formed by three distinct chemical routes, and the deuterium fractionation expected from each has been evaluated: hydrogenation of oxygen atoms on cold dust grains (e.g., Caselli et al. 2002), ion-molecule reactions in cold gas (e.g., Millar et al. 1989), and neutral-neutral reactions in hot shocked gas (Bergin et al. 1999). Observations of multiply deuterated molecules could in principle distinguish between gas-phase or grain-surface deuteration pathways (Rodgers & Charnley 2001). In the case of H_2O , measuring the abundance of heavy water (D_2O) could shed light on both the origin of water and the evolution of molecular clouds (Rodgers & Charnley 2002). In this Letter, we report the discovery of interstellar heavy water in absorption toward IRAS 16293–2422.

2. OBSERVATIONS

We observed the para- $D_2O(1_{10}-1_{01})$ fundamental transition at 316.799810 GHz using the James Clerk Maxwell Telescope (JCMT)⁷ in the direction of IRAS 16293–2422, at the nominal position $\alpha = 16^h32^m22.9^s$, $\delta = -24^\circ28'36.0''$ (J2000.0), which coincides with the A component of the binary system forming IRAS 16293–2422. The observations were obtained between 2005 March and July. The line was observed with the 345 GHz SIS receiver RxB3 in dual-channel single-sideband (SSB) mode using the lower sideband. Typical SSB temperatures were between 550 and 750 K. The observations were made in position-switched mode using a reference position $800''$ east of IRAS 16293–2022 with frequent pointing checks using the standard JCMT continuum position for IRAS 16293–2422. The Digital Autocorrelator Spectrometer back end was split into two sections of 125 MHz with a spectral resolution of 156 kHz, corresponding to an effective resolution of 0.18 km s^{-1} at 316.8 GHz. At 316.8 GHz, the FWHM beamwidth of the JCMT is about $15''$

⁷ The JCMT is operated by the Joint Astronomy Centre in Hilo, Hawaii, on behalf of the present organizations: the Particle Physics and Astronomy Research Council in the UK, the National Research Council of Canada, and the Netherlands Organization for Scientific Research.

TABLE 1
DERIVED LINE PARAMETERS FOR IRAS 16293–2422

Line	$\int T_{mb} dv$ (mK km s ⁻¹)	T_{peak} (mK)	ΔV (km s ⁻¹)	V_{LSR} (km s ⁻¹)
D_2O	-104 (25) 574 (75)	-184 (4) 88 (4)	0.53 (0.15) 6.13 (0.82)	4.09 (0.04) 4.09

NOTE.—Entries refer to the two-Gaussian components fitted.

with a main-beam efficiency (η_{mb}) of 63%. We have observed IRAS 16293–2422 for about 30,000 s, reaching $1 \sigma \text{ rms} = 37 \text{ mK}$ on a single channel. Scans were co-added to produce T_A^* , which was then converted to T_{mb} .

2.1. The D_2O Spectrum

Figure 1 shows the resulting JCMT spectrum after subtraction of the 850 mK continuum level (which was found to be consistent with the background continuum observed by SCUBA). In the same figure, we also display the spectrum of the HDO fundamental transition at 464 GHz, obtained with JCMT by Stark et al. (2004) and Parise et al. (2005). The D_2O and HDO spectra are very similar: they both show a narrow absorption dip at the systemic velocity of IRAS 16293–2422 ($\sim 4.0 \text{ km s}^{-1}$) superimposed on an emission component whose width is about 6 km s^{-1} . In addition, the D_2O spectrum shows the presence of an emission line at about 10 km s^{-1} (see below). The reality of this line was checked by changing the tuning at a different frequency.

In order to derive the para- D_2O line-integrated intensity, we fitted the data with a two-component Gaussian model, fixing the line centers of the absorption and emission component according to that found for the HDO line (Stark et al. 2004; Parise et al. 2005). The results are shown in Figure 1 and reported in Table 1. Figure 1 also presents the residuals in the upper portion. One additional spectral component is present around 10 km s^{-1} , corresponding to a rest frequency of 316.793 GHz, when considering the systemic velocity ($\sim 4.0 \text{ km s}^{-1}$). We inspected the Jet Propulsion Laboratory spectroscopy database and the Cologne Database for Molecular Spectroscopy (Pickett et al. 1998; Müller et al. 2001) and identified a few candidate species. Ethanol (C_2H_5OH) has a line at the right frequency (316.793460 GHz), but the observed signal would imply an implausibly large ethanol column density, and so we discard this possibility. Dimethyl ether (CH_3OCH_3) and $SO^{17}O$, the next most plausible lines, would require velocity shifts of -1.2 and $+3.9 \text{ km s}^{-1}$, respectively, from the nominal core V_{LSR} to match the observed line profile. In addition, the column density of both species would be 10 times larger than those derived by previous observations (Cazaux et al. 2003; Wakelam et al. 2004). We therefore consider these identifications to be highly unlikely. On the other hand, the line intensity of the $CH_3OD(7_0-6_0+)$ transition at 316.795074 GHz (Walsh et al. 2000) is in agreement with the previous detection of this molecule in IRAS 16293–2422 (Parise et al. 2002), and we therefore consider this to be the likely identification.

The presence of the D_2O line and the line at 10 km s^{-1} are confirmed by earlier lower spectral resolution data obtained with the Caltech Submillimeter Observatory (CSO) 10 m telescope on 2001 August 1. The spectra were taken in chopping secondary mode with a chop throw of $90''$. The back end used was an acousto-optical spectrometer with 500 MHz bandwidth, providing a velocity resolution of 1.33 km s^{-1} . The beam efficiency at 316 GHz was measured to be 0.75, and the beam size is $22''$. The system temperature was typically 1000 K, and an rms of 15 mK was reached after 60 minutes of integration.

The integrated line intensities measured at CSO are about a factor 2 lower than those measured at JCMT; within the calibration uncertainties ($\sim 20\%$), this is consistent with the emission of both lines originating in a region of size equal to or smaller than the JCMT beam. Given their higher spectral resolution, only the JCMT measurements are presented here.

In summary, using the velocity parameters of the known HDO emission, we can reproduce both the absorption feature and most of the broad emission centered around the nominal source velocity for the D₂O line at 316.8 GHz. Another feature appears at about 10 km s⁻¹ due to CH₃OD.

2.2. Column Density and D/H Ratios

Observations of singly deuterated water toward IRAS 16293–2422 show that it is abundant [$x(\text{HDO}) \sim 10^{-7}$]⁸ in the inner region of the envelope, where $T_{\text{dust}} \gtrsim 100$ K and ice mantles evaporate (Parise et al. 2005). In this region, the *hot corino*, the water fractionation ratio in the *evaporated ices* is estimated to be HDO/H₂O $\approx 3\%$.

The association of the HDO emission with the hot corino is based on a full radiative transfer model of IRAS 16293 (Parise et al. 2005). This considered several HDO lines and employed temperature and density profiles that have been validated by independent observations of the gas and dust emission (Ceccarelli et al. 2000; Schöier et al. 2002). These calculations show that HDO emission from the hot gas dominates because the abundance of HDO is so small [$x(\text{HDO}) \leq 10^{-9}$] in the outer region of the envelope, where it is presumably frozen onto the grains. The observed D₂O line width (~ 5 km s⁻¹) is also consistent with an origin in the hot corino gas. Therefore, it is extremely unlikely that the observed D₂O line originates in the cold outer envelope and so, in the following, we assume that it also originates in the hot corino.

We assume that the deexcitation collision coefficient for the D₂O($1_{10}-1_{01}$) transition is equal to 2.9×10^{-10} s⁻¹, the same value as that of the transition from the first excited state to the ground state of ortho-H₂O resulting from collisions with ortho-H₂ at a temperature of 100 K (Green et al. 1993). The corresponding critical density is $\sim 2 \times 10^6$ cm⁻³. For the physical conditions observed in the hot corino, i.e., a density of $\sim 3 \times 10^7$ cm⁻³ and a temperature of ~ 100 K (Ceccarelli et al. 2000) in a region 1.5'' in diameter (Kuan et al. 2004; Bottinelli et al. 2004), we can assume that the level populations are likely to be thermalized. This gives a para-D₂O column density, $N(\text{p-D}_2\text{O})$, of 3.5×10^{12} cm⁻². Further assuming the thermal equilibrium value 1 : 2 for the o-D₂O/p-D₂O ratio yields the total column of emitting D₂O molecules: $N(\text{D}_2\text{O}) = 1.0 \times 10^{13}$ cm⁻². Adopting $N(\text{H}_2) = 6 \times 10^{22}$ cm⁻² (Ceccarelli et al. 2000) gives a D₂O fractional abundance equal to 1.7×10^{-10} and corresponding fractionation ratios of D₂O/HDO ~ 0.0017 and D₂O/H₂O $\sim 5 \times 10^{-5}$. As discussed above, the D₂O line presents a dip of absorption at the systemic velocity of the source, with a measured line-to-continuum ratio equal to about 0.22 and a line width of 0.6 km s⁻¹. Assuming that all molecules are in the ground-state level, then $N(\text{p-D}_2\text{O}) \approx 2.8 \times 10^{12}$ cm⁻² is required to account for this absorption, in good agreement with the column density derived from the emission line. Finally, we emphasize that the observed D₂O line profile—emission on a ~ 5 km s⁻¹ range with absorption on a ~ 0.5 km s⁻¹ range—is similar to what is observed in many other molecular lines from IRAS 16293, including the HDO line shown in Figure 1. This profile is fully consistent with

the interpretation that the D₂O emission originates in the hot corino and is self-absorbed.

3. DISCUSSION

The observed D₂O, HDO, and H₂O molecules trace mantle material that has recently sublimated from dust grains. Postsublimation, gas-phase processes take $\sim 10^5$ yr to alter the D/H ratios in the sublimated species (Rodgers & Millar 1996). Typical estimates of the chemical ages of hot cores/corinos are lower than this ($\sim 10^4$ yr; Charnley et al. 1992) and, for the particular case of the IRAS 16293–2422 hot corino, could be much lower, $\sim 10^2$ – 10^3 yr (Wakelam et al. 2005). Therefore, the observed molecular D/H ratios in the hot corinos will be equal to those in the ice and will reflect the formation processes in the preceding cold, prestellar phase. Bergin et al. (1999) showed that the low HDO/H₂O ratios seen in massive hot cores ($\sim 10^{-4}$) could be understood if interstellar water is formed behind shock waves and condensed as ice. In IRAS 16293–2422, the observed HDO/H₂O ratio of 0.03 rules out this possibility (Parise et al. 2005) and, in conjunction with our value for D₂O/HDO of 1.7×10^{-3} , can be used to further constrain the chemical origin of the water.

3.1. Grain Surface Reactions?

If water forms via grain surface hydrogenation of O atoms, then H₂O, HDO, and D₂O will form contemporaneously, and the abundance ratios will be controlled by the relative accretion rates of D and H atoms. This ratio, r say, is dependent only on the gas-phase number densities of D and H atoms and is equal to $n(\text{D})/\sqrt{2}n(\text{H})$. If surface reactions distribute D statistically (cf. Watanabe 2005), then we will have HDO/H₂O and D₂O/H₂O ratios of $2r$ and r^2 , respectively. This assumes that the ratio r is constant over time; a more realistic calculation that accounts for the fact that r may vary with time results in the inequality

$$\left(\frac{\text{D}_2\text{O}}{\text{HDO}}\right)_{\text{grain}} \geq \frac{1}{4} \left(\frac{\text{HDO}}{\text{H}_2\text{O}}\right)_{\text{grain}}. \quad (1)$$

Using HDO/H₂O ≈ 0.03 (Parise et al. 2005), equation (1) predicts D₂O/HDO greater than 7.5×10^{-3} , in agreement with the value found in numerical models (0.01; Brown & Millar 1989) but ≈ 5 times higher than the observed ratio. It is unlikely that the D₂O/HDO ratio is wrong by this factor (the uncertainty in the H₂ column density cancels out). On the other hand, our HDO/H₂O ratio could be an overestimate if the H₂O abundance is actually 5 times larger than that reported by Parise et al. (2005). Because the H₂O lines are optically thick, it is possible that this could be the case (see discussion in Ceccarelli et al. 2000 and in Parise et al. 2005). However, we must conclude that, at present, the published data do not support an origin in grain-surface chemistry.

3.2. Gas-Phase Ion-Molecule Reactions?

Water formation via cold ion-molecule chemistry is initiated by proton transfer from H₃⁺ to atomic oxygen. HDO is formed simultaneously with H₂O via deuteron transfer from H₂D⁺ (as well as HD₂⁺ and D₃⁺), and we derive HDO/H₂O $\approx \bar{R}$, where \bar{R} is the overall D/H ratio in isotopologues of H₃⁺. The DCO⁺/HCO⁺ ratio will also be equal to \bar{R} , so the HDO/H₂O ratio derived by Parise et al. (2005) is consistent with the DCO⁺/HCO⁺ ratios seen in a number of dark clouds (≈ 0.03 – 0.06 ;

⁸ The value x is the fractional abundance relative to H₂.

Butner et al. 1995). D₂O, however, is not formed until much later in the chemical evolution of the cloud, via deuteron transfer to the HDO formed earlier, and so the D₂O/HDO ratio is a strong function of time, unlike the HDO/H₂O ratio, which is always very close to \bar{R} . Eventually, a chemical steady state is reached in which D₂O/HDO $\approx 0.2\bar{R}$ (Rodgers & Charnley 2002), but chemical models show that this can take almost 1 Myr (Roberts & Millar 2000). Therefore, for ion-molecule chemistry we derive

$$\left(\frac{\text{D}_2\text{O}}{\text{HDO}}\right)_{\text{im}} \leq \frac{1}{5} \left(\frac{\text{HDO}}{\text{H}_2\text{O}}\right)_{\text{im}} \quad (2)$$

Again, using HDO/H₂O = 0.03, we predict a maximum value for the D₂O/HDO ratio of 0.006, consistent with the observed value, which is 3.5 times less. This suggests that the material forming the IRAS 16293–2422 system did not have time to reach a chemical steady state and only underwent dense chemical evolution for a few times 10⁵ yr before the water molecules froze out, as expected in the free-fall collapse of a prestellar core (Brown et al. 1988).

4. CONCLUSIONS

We have detected heavy water (D₂O) in an astronomical environment for the first time. In IRAS 16293–2422, we determine a total D₂O column density of $1.0 \times 10^{13} \text{ cm}^{-2}$ and a fractional abundance of D₂O/H₂ = 1.7×10^{-10} . The derived deuterium fractionation ratios are D₂O/HDO = 1.7×10^{-3} and D₂O/H₂O = 5×10^{-5} . Shock chemistry can be ruled out

as contributing to the origin of the water in this source. At steady state, grain-surface chemistry and ion-molecule reactions both predict D₂O/HDO ratios ≈ 4 –5 times higher than observed. However, in the latter case, lower D₂O/HDO ratios are possible if the gas-phase chemistry of water and its deuterated isotopologues did not attain a chemical steady state prior to most of the molecules condensing onto dust grains. This scenario is also consistent with the low fractional abundance of water measured in IRAS 16293–2422 and is generally consistent with rapid molecular cloud formation and protostellar evolution (di Francesco et al. 2007; Ceccarelli et al. 2007).

As it is becoming clear that extreme deuteration appears to be common around low-mass protostars (Ceccarelli et al. 2007; Parise et al. 2006), it is likely that the D₂O/HDO/H₂O ratios can be determined in other sources and so shed further light on the chemistry of interstellar isotopic fractionation. Multi-transition observations of additional sources are also needed to obtain reliable H₂O abundances (Maret et al. 2002), and so the *Herschel Space Observatory* will provide a breakthrough in this respect.

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