Note

Hyperfine structure of $H_2^{16}O$ and $H_2^{18}O$ measured by Lamb-dip technique in the 180–560 GHz frequency range

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In the following note we report the measurements in the millimeter and submillimeter region of the hfs-spectra of some ortho-water transition lines followed by precise measurements of line center frequencies of a few para-water transition lines. The assignment of the ortho and para states was experimentally verified for some lines.

Although hfs-spectra of water isotopologues have been extensively studied in the microwave region, only the hf-structures of two lines of $H_2^{17}O$ and D_2O have been measured in the mm-wave range [1,2]. The hf-components of the rotational transition $J'_{K'_-K'_+} \leftarrow J''_{K''_-K''_+} = 3_{13}-2_{20}$ of $H_2^{17}O$ in [1] was resolved by conventional absorption spectroscopy because of the large quadrupole moment of the ^{17}O nucleus ($I = 5/2$); in [2] molecular beam maser spectroscopy was extended into submillimeter region and it allowed to resolve the deuterium hfs-splittings of the $1_{10}-1_{01}$ line of D_2O near 317 GHz. The hf-structure of the transition $6_{16}-5_{23}$ of $H_2^{18}O$ has not been resolved even if it lies in the microwave region [3]. The spectral measurements of $H_2^{16}O$ and $H_2^{18}O$ in millimeter and submillimeter regions are given in [4,5] with a quoted accuracy of 150 kHz as far as the line center measurement concerns. The $3_{13}-2_{20}$ line ($H_2^{16}O$) was measured with an accuracy of 2 kHz (Lamb-dip measurement of Winton [6] quoted as Ref. [15] in Table 1 of [4]). Its center given as 183310.117(2) MHz is outside of the error range found by the measurements in [7] as 183310.0906(15) MHz and in [8] as 183310.075(5) MHz, respectively. The recent improvement of the spectrometer at the Technische Fakultät der Universität zu Kiel with the application of the Lamb-dip

absorption technique (ISTOK BWOs are used as radiation sources) allowed to re-measure the frequency of this line as 183310.087 MHz with an accuracy of ±1 kHz (one standard deviation). Some details of the spectrometer and considerations about accuracy of the measurements were given in [9]. A spectrometer frequency resolution, determined by the width of a Lamb-dip (half-width was in the order of 30 kHz at pressures of 0.5–1 mTorr), allowed us to observe also hfs-components of following water vapor isotopologues: $H_2^{16}O$, $H_2^{17}O$, $H_2^{18}O$, HDO and D_2O. In the present note, we report the measurements of $H_2^{16}O$ and $H_2^{18}O$ lines performed in the 180–560 GHz frequency range.

Lines of ortho-water (total spin of protons $I = 1/2 + 1/2 = 1$) exhibit hyperfine structure due to the coupling of the proton nuclear spins with the rotational angular momentum ($\mathbf{I \cdot J}$), and to a direct spin–spin interaction ($\mathbf{I \cdot I}$). Para-water (total spin of protons $I = 0$) has no hfs-structure. The coupling scheme is $\mathbf{F = I + J}$, $\mathbf{F}$ is the total angular momentum. The energy level is splitted on three sub-levels $F = J - 1, J, J + 1$ and has the form

$$E = \frac{C(J_{K-,K+})}{2} \cdot [F(F + 1) - I(I + 1) - J(J + 1)] + 4D(J_{K-,K+}) \cdot Y(I, J, F),$$

where $Y(I, J, F)$ is the Casimir's function [10,11]. The spin-rotational $C(J_{K-,K+})$ and spin–spin $D(J_{K-,K+})$ constants are dependent on the rotational level $J_{K-,K+}$, and defined as follows (we used expressions as in [12,13]):

$$C(J_{K-,K+}) = \sum_g [C_{gg}\langle J_g^2\rangle / J(J + 1)],$$

$$D(J_{K-,K+}) = \frac{1}{2}\frac{\mu_N^2 g_I^2}{R^3}\left(1 - 3\sum_g [\alpha_g^2\langle J_g^2\rangle / J(J + 1)]\right),$$

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Table 1
The frequencies of the rotational $H_2^{16}O$ lines measured in present and previous works[a]

Transition $J'_{K'_-K'_+} \leftarrow J''_{K''_-K''_+}$	Frequency (MHz), this work	Line center of gravity (calc.)	Frequency (MHz), from Ref. [ ]
(ortho) $6_{16}-5_{23}$		22235.079846	22235.04400(5) [12]
			22235.07706(5) [12]
			22235.12036(5) [12]
			22235.25300(214) [12]
			22235.29770(215) [12]
(para) $3_{13}-2_{20}$	183310.087(1)	183310.087(1)	183310.0906(15) [7]
			183310.117(2) [6]
			183310.075 (5) [8]
(ortho) $10_{29}-9_{36}$	321225.642(4)	321225.676(6)	321225.644(150) [4]
	321225.679(4)		
	321225.712(4)		
(para) $5_{15}-4_{22}$	325152.899(1)	325152.899(1)	325152.919(150) [4]
(ortho) $4_{14}-3_{21}$	380197.337(2)	380197.356(5)	380197.372(150) [4]
	380197.409(2)		
(para) $7_{53}-6_{60}$	437346.664(2)	437346.664(2)	437346.667(150) [4]
(ortho) $6_{43}-5_{50}$	439150.775(2)	439150.795(5)	439150.812(150) [4]
	439150.844(2)		
(ortho) $7_{52}-6_{61}$	443018.337(2)	443018.355(5)	443018.295(150) [4]
	443018.398(2)		
(ortho) $4_{23}-3_{30}$	448001.055(2)	448001.075(5)	448001.075(150) [4]
	448001.132(2)		
(para) $6_{42}-5_{51}$	470888.903(2)	470888.903(2)	470888.947(150) [4]
(para) $5_{33}-4_{40}$	474689.108(1)	474689.108(1)	474689.127(150) [4]
(para) $6_{24}-7_{17}$	488491.128(3)	488491.128(3)	488491.133(150) [4]
(ortho) $8_{63}-7_{70}$	503568.520(20)	503568.520(20)	
(ortho) $1_{10}-1_{01}$	556935.995(15)	556935.995(15)	556936.002(150) [4]

[a] Uncertainties given in parenthesis are in units of the last digit; the values reported in this work are correspondent to one standard deviation as result of having averaged out many line records taken up at different conditions.

where μ_N and g_I are the nuclear magneton and the g-factor of the two equivalent nuclei, respectively; R is the distance between the two nuclei, α_g are the cosines of the angle between the vector joining both equivalent nuclei and the principal axes of the molecule; $\langle J_g^2 \rangle$ are the average values of the square components of J along the principal axes [14]. For $\langle J_g^2 \rangle$ calculations we used the values of energy levels E_{K_-,K_+} of a rigid rotor listed in Appendix IV of [10]. Intensities of hf-lines are calculated using the formula given in [11,14]. For molecules in $^1\Sigma$-state, under assumption of the rigid rotor model, the tensor diagonal elements C_{gg} are independent of the rotational state of the molecule and considered as molecular constants. The C_{gg} values based on microwave lines measurements of $H_2^{16}O$, HDO and D_2O were calculated in [13] as $C_{aa} = -35.14(15)$, $C_{bb} = -30.68(30)$ and $C_{cc} = -32.68(16)$ kHz. The list of C_{gg} values calculated using the program DALTON is also given in [15].

Practically, all $H_2^{16}O$ and $H_2^{18}O$ ortho-water lines observed by us in the reported frequency range exhibit two peaks: the lower frequency peak is approximately 3–4 times stronger than the higher frequency one. The separation between the two peaks is within 60–85 kHz.

The splitting of ortho-H_2O levels into three hfs-sublevels gives six hfs-components. From theoretical estimations of hfs-patterns the two strongest lines ($F' = J' + 1 - F'' = J'' + 1$, $F' = J' - F'' = J''$) fall within 20 kHz and exhibit the lower frequency peak (note that our spectrometer resolution of 30 kHz did not allow to resolve these two closed
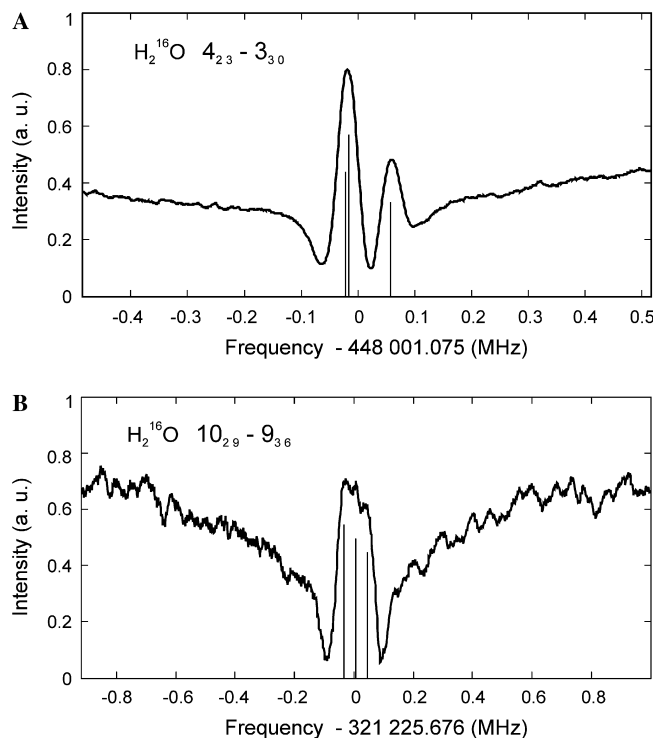
Fig. 1. Lamb-dip records of the $J'_{K'_-K'_+} \leftarrow J''_{K''_-K''_+} = 4_{23}-3_{30}$ at 448001.075 MHz (A) and $10_{29}-9_{36}$ at 321225.676 MHz (B) lines of $H_2^{16}O$. Frequency modulation and $2f$ detection were used, the lines represent the Lorentz shape saturation dips (half-width is about 30 kHz at pressures of about 1 mTorr) in Doppler profile. The vertical lines below the traces show the calculation result of the three strongest hf-components ($F' - F'' = 5-4$, $4-3$, $3-2$ and $F' - F'' = 11-10$, $10-9$, $9-8$).

Table 2
The frequencies of the $H_2^{18}O$ lines[a]

Transition $J'_{K'_\perp K'_\perp} \leftarrow J''_{K''_\perp K''_\perp}$	Frequency (MHz), this work	Line center of gravity (calc.)	Frequency (MHz), from Ref. [ ]
(ortho) 6_{16}–5_{23}			5625.147(15) [3]
(para) 3_{13}–2_{20}	203407.498(4)	203407.498(4)	203407.52(2) [5]
(ortho) 10_{29}–9_{36}	253913.273(5)	253913.309(7)	
	253913.310(5)		
	253913.347(5)		
(para) 5_{15}–4_{22}	322465.122(2)	322465.122(2)	322465.17(5) [5]
(ortho) 4_{14}–3_{21}	390607.757(2)	390607.776(4)	390607.76(4) [5]
	390607.831(2)		
(ortho) 4_{23}–3_{30}	489054.228(2)	489054.250(4)	489054.26(8) [5]
	489054.313(2)		
(ortho) 1_{10}–1_{01}	547676.470(15)	547676.470(15)	547676.44(6) [5]

[a] Uncertainties given in parenthesis are in units of the last digit; the values reported in this work are correspondent to one standard deviation as result of having averaged out many line records taken up at different conditions.

hfs-lines). The third line ($F' = J' - 1 - F'' = J'' - 1$) is separated from them about of 70 kHz and is correspondent to the higher frequency peak. This assignment is consistent with line intensities and the line widths—the lower frequency peak is broader by 10–15 kHz than higher frequency peak. The other three *hfs*-components are too weak to be observed (they lie approximately at 100–600 kHz higher than the observed lines). Fig. 1A represents the typical ortho-water spectrum where the record of 4_{23}–3_{30} transition of $H_2^{16}O$ near 448 GHz is shown (the calculated positions of *hfs*-lines with calculated intensities are marked by the vertical lines).

We fit our data together with the *hf*-frequencies of the 6_{16}–5_{23} line near 22 GHz [12,16]. The $D(J_{K-,K+})$ constants are calculated from the molecular geometry. The obtained tensor diagonal element values are $C_{aa} = -33.3(4)$, $C_{bb} = -31.3(3)$ and $C_{cc} = -33.0(3)$ kHz, respectively; the average line prediction uncertainty is about 2 kHz. In comparison with the data obtained in [13] our C_{aa} value is smaller by 1.8 kHz. It should be noted, that in [13] the *hfs*-structure of the line 6_{16}–5_{23} of $H_2^{16}O$ only was used for the C_{gg} calculations.

Based on these newly obtained C_{gg} values, predictions of the $H_2^{18}O$ *hf*-patterns should be very close to the separations between *hfs*-lines of the corresponding $H_2^{16}O$ transitions, but the measurements show that the separations between two peaks for $H_2^{18}O$ are a little larger than for $H_2^{16}O$. For instance, for the 4_{23}–3_{30} line of $H_2^{18}O$ it is about 10 kHz larger in comparison with our estimations. Unfortunately, we have no sufficient frequency resolution and enough lines to make an unambiguous fit to obtain the spin-rotational constants of $H_2^{18}O$ molecule. The discrepancies could also be due to the consideration of the $H_2^{16}O$ molecule as a rigid rotator for our theoretical calculation. As it was also noted in [12] the calculated spin–spin interaction coefficients $D(J_{K-,K+})$ for the 6_{16} and 5_{23} energy levels were larger by about of 8% (three times the experimental error) than those obtained as result of a fit.

Further analysis of water vapor *hf*-spectra will be given in a forthcoming paper about our measurements of HDO and D_2O lines in the 180–560 GHz frequency range.

In Tables 1 and 2 some frequencies of $H_2^{16}O$ and $H_2^{18}O$ lines measured in this work are listed for comparison together with those reported in earlier papers. Since the "center of gravity" of an energy level is not shifted in *hfs*-splitting, in the 3rd columns of the tables the calculated values of line "centers of gravity" are given. The line 1_{10}–1_{01} of $H_2^{16}O$ has three strong components ($F' - F'' = 2$–1, 2–2, and 1–1) separated respect to the line "center of gravity" by −48.9, −5.3, and +26.0 kHz. Due to the cross-over effect [17–20] there are also "ghost" lines in between the pattern, so we could not resolve it. The line 10_{29}–9_{36} has *hfs*-components at −39.2, 0.2 and +40.4 kHz ($F' - F'' = 11$–10, 10–9, 9–8) as shown in Fig. 1B. The resolution for this line is poor because of the line weakness, but the line pattern is in agreement with the calculations. Two lines listed in the tables were measured by conventional absorption technique (8_{63}–7_{70} of $H_2^{16}O$ and 1_{10}–1_{01} of $H_2^{18}O$).

Highly accurate laboratory spectra of the water molecule are relevant to its astrophysical observations as from maser sources [21,22], comets [23], planets [24] and interstellar clouds [25,26].

References

[1] F.C. De Lucia, P. Helminger, J. Mol. Spectrosc. 56 (1975) 138–145.
[2] Garvey, R. Michael, F.C. De Lucia, Can. J. Phys. 55 (1977) 1115–1123.

[3] F.X. Powell, D. Johnson, Phys. Rev. Lett. 24 (12) (1970) 637.

[4] F.C. De Lucia, P. Helminger, R.L. Cook, W. Gordy, Phys. Rev. A 5 (2) (1972) 487–490.

[5] F.C. De Lucia, P. Helminger, R.L. Cook, W. Gordy, Phys. Rev. A 6 (4) (1972) 1324–1326.

[6] R.S. Winton, PhD Dissertation (Duke University, 1972) unpublished.

[7] C. Huiszoon, Rev. Sci. Instrum. 42 (4) (1971) 477–481.

[8] G.Yu. Golubiatnikov, J. Mol. Spectrosc. 230 (2005) 196–198.

[9] G.Yu. Golubiatnikov, A.V. Lapinov, A. Guarnieri, R. Knöchel, J. Mol. Spectrosc. 234 (2005) 190–194.

[10] C.H. Townes, A.L. Schawlow, Microwave spectroscopy, Dover Publications, Inc., New York, 1975.

[11] W. Gordy, R.L. Cook, Microwave Molecular Spectra, John Wiley, New York, 1984.

[12] S.G. Kukolich, J. Chem. Phys. 50 (1969) 3751–3755.

[13] H. Bluyssen, A. Dymanus, J. Reuss, J. Verhoeven, Phys. Lett. 25A (8) (1967) 584–585.

[14] P. Thaddeus, L.C. Krisher, J.H.M. Loubser, J. Chem. Phys. 40 (1964) 257–273.

[15] A. Miani, J. Tennyson, J. Chem. Phys. 120 (2004) 2732–2739.

[16] H. Bluyssen, A. Dymanus, J. Verhoeven, Phys. Lett. 24A (9) (1967) 482–483.

[17] V.S. Letokhov, Saturation spectroscopy, in: K. Shimoda (Ed.), High-Resolution Laser Spectroscopy, Topics Appl. Phys., vol. 13, Springer, Berlin, 1976.

[18] A.H. Paxton, P.W. Milonni, Phys. Rev. A 26 (1982) 1549.

[19] S. Mandal, P.N. Ghosh, Phys. Rev. A 45 (1992) 4990.

[20] W. Demtröder, Laserspektroskopie, Springer, Verlag, Berlin, 1982.

[21] D.A. Varshalovich, A.V. Ivanchik, N.S. Babkovskaya, Astron. Lett. 32 (1) (2006) 29–38 (published in Pis'ma v Astronomicheskii Zhurnal 32(1) (2006) 32–41 in Russian).

[22] W.H.T. Vlemmings, H.J. van Langevelde, Astron. Astrophys. 434 (2005) 1021–1028.

[23] D. Bockelée-Morvan, N. Biver, P. Colom, et al., Icarus 167 (2004) 113–128.

[24] N. Biver, A. Lecacheux, T. Encrenaz, et al., Astron. Astrophys. 435 (2005) 765–772.

[25] J. Cernicharo, J.R. Pardo, E. González-Alfonso, et al., Astrophys. J. 520 (1999) L131–L134.

[26] F. Combes, T. Wiklind, Astrophys. J. 486 (1997) L79–L82.