

## Note

# Hyperfine structure of $\text{H}_2^{16}\text{O}$ and $\text{H}_2^{18}\text{O}$ measured by Lamb-dip technique in the 180–560 GHz frequency range

G.Yu. Golubiatnikov <sup>a,\*</sup>, V.N. Markov <sup>a</sup>, A. Guarnieri <sup>b,c</sup>, R. Knöchel <sup>b</sup>

<sup>a</sup> Institute for Applied Physics of the Russian Academy of Sciences, 46 Uljanova st., GSP-120, 603950 Nizhnii Novgorod, Russia

<sup>b</sup> Technische Fakultät der Christian-Albrechts-Universität zu Kiel, Lehrstuhl für Hochfrequenztechnik, Kaiserstraße 2, Kiel D-24143, Germany

<sup>c</sup> Institut für Physikalische Chemie der Christian-Albrecht-Universität zu Kiel, Ludwig-Meyn-Str. 8, 24118 Kiel, Germany

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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  $\text{H}_2^{17}\text{O}$  and  $\text{D}_2\text{O}$  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  $\text{H}_2^{17}\text{O}$  in [1] was resolved by conventional absorption spectroscopy because of the large quadrupole moment of the  $^{17}\text{O}$  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  $\text{D}_2\text{O}$  near 317 GHz. The *hf*-structure of the transition  $6_{16-5_{23}}$  of  $\text{H}_2^{18}\text{O}$  has not been resolved even if it lies in the microwave region [3]. The spectral measurements of  $\text{H}_2^{16}\text{O}$  and  $\text{H}_2^{18}\text{O}$  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 ( $\text{H}_2^{16}\text{O}$ ) 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  $\pm 1$  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:  $\text{H}_2^{16}\text{O}$ ,  $\text{H}_2^{17}\text{O}$ ,  $\text{H}_2^{18}\text{O}$ , HDO and  $\text{D}_2\text{O}$ . In the present note, we report the measurements of  $\text{H}_2^{16}\text{O}$  and  $\text{H}_2^{18}\text{O}$  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 ( $\mathbf{I} \cdot \mathbf{J}$ ), and to a direct spin–spin interaction ( $\mathbf{I} \cdot \mathbf{I}$ ). Para-water (total spin of protons  $I=0$ ) has no *hfs*-structure. The coupling scheme is  $\mathbf{F}=\mathbf{I}+\mathbf{J}$ ,  $\mathbf{F}$  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]):

\* Corresponding author. Fax: +7 8312 363792.

E-mail addresses: [glb@appl.sci-nnov.ru](mailto:glb@appl.sci-nnov.ru) (G.Yu. Golubiatnikov), [ag@tf.uni-kiel.de](mailto:ag@tf.uni-kiel.de) (A. Guarnieri).

Table 1  
The frequencies of the rotational  $\text{H}_2^{16}\text{O}$  lines measured in present and previous works<sup>a</sup>

| 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]<br>22235.07706(5) [12]<br>22235.12036(5) [12]<br>22235.25300(214) [12]<br>22235.29770(215) [12] |
| (para) $3_{13}-2_{20}$                               | 183310.087(1)                                   | 183310.087(1)                  | 183310.0906(15) [7]<br>183310.117(2) [6]<br>183310.075(5) [8]   |
| (ortho) $10_{29}-9_{36}$                             | 321225.642(4)<br>321225.679(4)<br>321225.712(4) | 321225.676(6)                  | 321225.644(150) [4]   |
| (para) $5_{15}-4_{22}$                               | 325152.899(1)                                   | 325152.899(1)                  | 325152.919(150) [4]   |
| (ortho) $4_{14}-3_{21}$                              | 380197.337(2)<br>380197.409(2)                  | 380197.356(5)                  | 380197.372(150) [4]   |
| (para) $7_{53}-6_{60}$                               | 437346.664(2)                                   | 437346.664(2)                  | 437346.667(150) [4]   |
| (ortho) $6_{43}-5_{50}$                              | 439150.775(2)<br>439150.844(2)                  | 439150.795(5)                  | 439150.812(150) [4]   |
| (ortho) $7_{52}-6_{61}$                              | 443018.337(2)<br>443018.398(2)                  | 443018.355(5)                  | 443018.295(150) [4]   |
| (ortho) $4_{23}-3_{30}$                              | 448001.055(2)<br>448001.132(2)                  | 448001.075(5)                  | 448001.075(150) [4]   |
| (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]   |

<sup>a</sup> 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.

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

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

where  $\mu_N$  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,  $\alpha_g$  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  $\text{H}_2^{16}\text{O}$ , HDO and  $\text{D}_2\text{O}$  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  $\text{H}_2^{16}\text{O}$  and  $\text{H}_2^{18}\text{O}$  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.

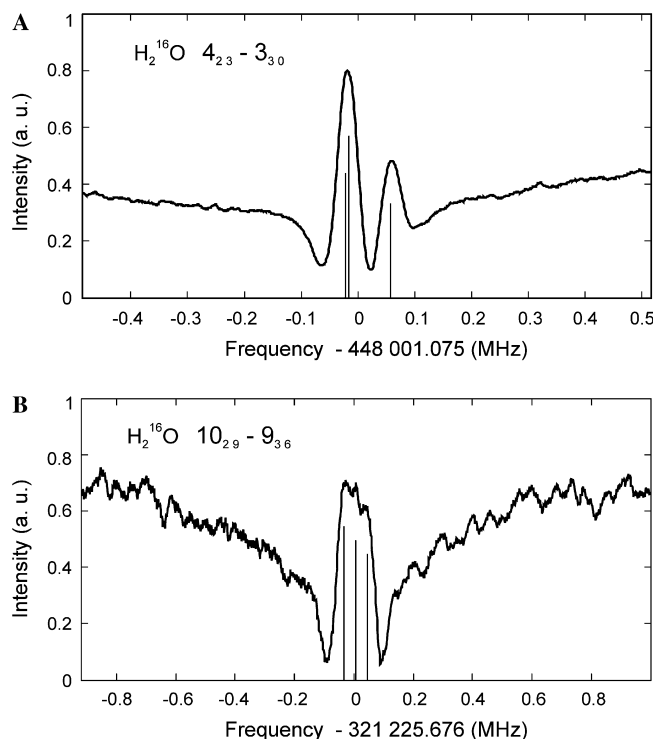


Fig. 1. Lamb-dip records of the  $J'_{K'-K'_+} \leftarrow J''_{K''-K''_+} = 4_{23}-3_{30}$  at 448001.075 MHz (A) and  $10_{29}-9_{36}$  at 321225.676 MHz (B) lines of  $\text{H}_2^{16}\text{O}$ . Frequency modulation and  $2f$  detection were used, the lines represent the Lorentz shape saturation dips (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<sub>2</sub><sup>18</sup>O lines<sup>a</sup>

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

<sup>a</sup> 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.

The splitting of ortho-H<sub>2</sub>O 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 *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<sub>23</sub>–3<sub>30</sub> transition of H<sub>2</sub><sup>16</sup>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<sub>16</sub>–5<sub>23</sub> 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<sub>16</sub>–5<sub>23</sub> of H<sub>2</sub><sup>16</sup>O only was used for the  $C_{gg}$  calculations.

Based on these newly obtained  $C_{gg}$  values, predictions of the H<sub>2</sub><sup>18</sup>O *hf*-patterns should be very close to the separations between *hfs*-lines of the corresponding H<sub>2</sub><sup>16</sup>O transitions, but the measurements show that the separations between two peaks for H<sub>2</sub><sup>18</sup>O are a little larger than for H<sub>2</sub><sup>16</sup>O. For instance, for the 4<sub>23</sub>–3<sub>30</sub> line of H<sub>2</sub><sup>18</sup>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<sub>2</sub><sup>18</sup>O molecule. The discrepancies could also be due to the consideration of the H<sub>2</sub><sup>16</sup>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<sub>16</sub> and 5<sub>23</sub> 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<sub>2</sub>O lines in the 180–560 GHz frequency range.

In Tables 1 and 2 some frequencies of H<sub>2</sub><sup>16</sup>O and H<sub>2</sub><sup>18</sup>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<sub>10</sub>–1<sub>01</sub> of H<sub>2</sub><sup>16</sup>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<sub>29</sub>–9<sub>36</sub> 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<sub>63</sub>–7<sub>70</sub> of H<sub>2</sub><sup>16</sup>O and 1<sub>10</sub>–1<sub>01</sub> of H<sub>2</sub><sup>18</sup>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].

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