Frequency measurement of pure rotational transitions of D$_2$O using tunable terahertz spectrometer

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Abstract. Precise frequency measurement of the rotational lines of D$_2$O in the terahertz (far-infrared) region is demonstrated as a case study of a high-precision far-infrared spectroscopy using a tunable radiation source. Frequencies of about 150 rotational lines of D$_2$O were measured in the 0.5 - 5 THz region. Measured frequencies provide an excellent frequency standard for the terahertz region together with our measurements on H$_{16}$O (v=0 and v$_2$=1 vibrational states), H$_{17}$O, and H$_{18}$O. Molecular parameters of Watson's A-reduced Hamiltonian have been obtained to reproduce the observed frequencies.

1. Introduction
Precise spectroscopy of the H$_2$O molecule is important for researchers both in experiment and theory. Rotational spectra of water vapor, which have large density of lines and strong absorption intensity in the terahertz region, or in the other word, far-infrared (FIR) region, is a good calibration choice for the spectrometers in the terahertz region. Theoretical calculation of the energy levels of H$_2$O is still one of the challenging subject for theoreticians because the molecule is a typical example of light rotator with large centrifugal distortion effects.

In this paper, precise frequency measurement of the rotational lines of D$_2$O in the terahertz region is described as a case study of a high-precision far-infrared spectroscopy using a tunable terahertz spectrometer in Toyama. Other than D$_2$O, we measured frequencies of pure rotational transitions of H$_{16}$O (v=0 and v$_2$=1 vibrational states), H$_{17}$O, and H$_{18}$O in the frequency range from 0.5 to 5 THz [1-4].

Historically, low frequency rotational lines of D$_2$O have been measured by several groups using microwave spectrometers [5-13]. Up to 1985, the number of reported rotational lines was 66 in total and data were limited to the frequency range below 1100 GHz.

Frequencies of a number of rotational lines were measured by using Fourier transform (FT) spectrometers. Frequency table of D$_2$O was extended to 220 cm$^{-1}$ by the FT study of Johns in 1985 [14]. He also reported the measurements of other isotopic species of water molecule and gave the sets of molecular parameters for each species. The table was extended to 420 cm$^{-1}$ by Paso and Horneman in 1995 [15]. The spectral resolution of the FT spectrometer is typically about 0.0025 cm$^{-1}$.

In our work, rotational transitions of D$_2$O have been measured in the frequency range from 0.5 to 5.2 THz (16 to 173 cm$^{-1}$) with a frequency tunable terahertz spectrometer. Though
the range of the measurement overlaps with that of FT measurements, the accuracy of the frequency measurement has been improved to better than 100 kHz which is comparable with that of microwave measurements.

2. Experimental

The frequency tunable terahertz spectrometer used in the present work (referred to as TuFIR as a contracted form of "tunable far-infrared") is based on a frequency synthesizing technique developed by Evenson and co-workers [16]. The principle of the spectrometer can be found in the previous papers [16-17]. A schematics of the spectrometer is shown in Fig.1. Two CO$_2$ laser radiations, frequency of each laser denoted as $f_1$ and $f_2$, are mixed in a metal-insulator-metal (MIM) diode to generate a far-infrared radiation of high spectral purity with the difference frequency of $|f_1 - f_2|$. Then a microwave radiation tunable up to 18 GHz is fed to the MIM diode through a whisker to generate tunable sidebands. By denoting the frequency of the microwave radiation as $f_{MW}$, frequency of the obtained FIR sidebands, $f_{FIR}$, are $f_{FIR} = |f_1 - f_2| = f_{MW}$. The present spectrometer can synthesize terahertz radiation with the frequency up to 5.3 THz by using two lasers with normal CO$_2$ lasing gas. Though the output of the FIR radiation is as small as the order of 100 nW, it is enough to observe strong rotational lines of neutral molecules such as water molecule. A liquid-helium-cooled silicon composite bolometer is used to detect the FIR radiation.

The sample cell is a Pyrex glass tube of 1.5 m in length and 12 mm in diameter with polypropylene windows of 1mm thickness at each end. The D$_2$O sample of 99.75 percent enrichment was used. Most of the lines were observed at a pressure of about 1 mTorr or less. The path of the FIR radiation outside the sample cell was purged with nitrogen gas to prevent the absorption of FIR radiation by atmospheric water vapor.

![Figure 1. Schematic diagram of the tunable terahertz spectrometer.](image)

![Figure 2. Accidentally overlapped lines are well resolved with Doppler line width.](image)

3. Results and discussion

Though most of the rotational lines appear as an isolated single line, Figure 2. shows an unusual case of closely overlapped two lines near 3.367 THz. The lines in Fig. 2, $J_{70} \leftarrow J_{61}$ and $J_{71} \leftarrow J_{62}$, can not be resolved in the FT spectrometer but are now well resolved with Doppler line width.

Each spectral line shape was fitted by least squares program [18] to a theoretical Voigt profile to determine the line center. Two lines in Fig.2 were determined to be 3367260.541 (0.039)MHz and 3367279.136(0.037)MHz, respectively.
We picked up the candidate lines of our measurement from the frequency tables obtained by FT spectrometers previously [14,15]. Frequency of about 150 rotational lines of D$_2$O were determined. Table of the measured frequency can be found in reference [4]. The estimated uncertainty is below 50 kHz for most of the lines. The uncertainties of measured line positions are contributed by (i) the uncertainty of the synthesized FIR frequency and (ii) that in determining the center frequency of the spectral line. The uncertainty (i) is estimated to be about 35 kHz assuming the uncertainty of the frequency of each laser line to be 25 kHz. The uncertainty (ii) is contributed by several factors such as the noise in the absorption signal which mainly comes from detector noise, a deformation of the spectral line, and that of the base line.

Calculation of the energy term of water molecule based on Taylor-series Hamiltonian in the Watson form [19] leads to large errors because of the large centrifugal distortion effect of the molecule. Researchers proposed theories to improve the calculation of water molecule [20-21]. Nevertheless, a calculation using Taylor series Hamiltonian is still a convenient method for giving precise term values for the levels with low rotational quantum numbers. So, we used a Hamiltonian based on Watson’s A-reduction to reproduce our frequency data set. The Hamiltonian is shown as:

$$H = \frac{1}{2}(B + C)J^2 + \left( A - \frac{B + C}{2} \right)J_z^2 + \frac{1}{2}(B - C)J_{xy}^2 - \Delta_J(J^2)^2 - \Delta_{JK}J^2J_z^2 - \Delta_KJ_z^4$$

$$-2\delta_JJ_x^2J_y^2 - \delta_J\{J_x^2, J_y^2\} + H_J(J^2)^3 + H_{JK}(J^2)^2J_z^2 + H_KJ_z^4 + H_KJ_z^6$$

$$+2h_J(J^2)^2J_{xy}^2 + h_{JK}J_x^2\{J_y^2, J_{xy}\} + h_K\{J_x^4, J_{xy}^2\} + L_J(J^2)^4 + L_{JK}(J^2)^3J_z^2$$

$$+L_{JK}(J^2)^2J_z^4 + L_{KK}J_x^2J_z^6 + L_KJ_z^8 + 2f_J(J^2)^3J_{xy}^2 + f_{JK}(J^2)^2\{J_x^2, J_{xy}\}$$

$$+f_{JK}(J^2)^2J_x^2J_{xy}^2 + f_K\{J_x^6, J_{xy}^2\} + P_{KK}J_x^2J_z^8 + P_KJ_z^{10} + P_J(J^2)^4$$

$$+p_{JK}(J^2)^3\{J_x^2, J_{xy}^2\} + p_K\{J_z^8, J_{xy}^2\} + T_KJ_z^{12}$$

where

$$J_{xy}^2 = J_x^2 - J_y^2,$$

$$\{A, B\} = AB - BA.$$

The molecular parameters obtained for D$_2$O are shown in Table 1.

Historically, the parameters have been based on the microwave spectroscopy of pure rotational transitions [5,13,14,22,23] or infrared spectroscopy of vibration-rotation transitions [24]. Calculated frequencies using previous parameters had typical discrepancies of several megahertz from frequencies observed in the present work. Because the precise frequency data comparable to that of microwave spectrometer were obtained by the present TuFIR spectrometer up to 5 THz, the molecular parameters in the ground state were improved so that the discrepancies between the calculated and observed values are mostly within 50 kHz.

Recently, Furtenbacher and Császár examined the accuracy and consistency of our TuFIR data of water molecule using their protocol MARVEL (standing for Measured Active Rotational-Vibrational Energy Levels) [25]. The data of H$_2^16$O (ground state and v$_2$=1 state), H$_2^17$O, H$_2^18$O and D$_2^16$O were proved to have high accuracy and it was shown that the data can be candidates for becoming frequency standards in the FIR region of 15-170 cm$^{-1}$ (0.5-5THz).

The present TuFIR spectrometer has been used to investigate many kinds of molecules other than water molecule such as neutral molecule or radical (LiH, KH, $^{18}$OH), molecule with internal rotation (CH$_3$OH), molecular cation (HeH$^+$, NeH$^+$, ArH$^+$, KrH$^+$, XeH$^+$ (each including its isotopomers), H$_2$D$^+$), and molecular anion (OH$^-$, OD$^-$). These data obtained with the TuFIR spectrometer can be referenced by accessing the database “Toyama Microwave Atlas for spectroscopists and astronomers” which is maintained by the authors [26].
Table 1. Molecular parameters (in MHz) for the ground state of D$_2$O

| Parameter       | Value                  |
|-----------------|------------------------|
| A               | 462278.8077 (92)       |
|                  | $H_{KJ} \times 10^2$   |
|                  | -7.629 (18)            |
|                  | $\ell_J \times 10^7$   |
|                  | -2.05 (fixed)          |
| B               | 218038.2178 (78)       |
|                  | $H_K \times 10^4$      |
|                  | 5.5552 (15)            |
|                  | $\ell_J \times 10^6$   |
|                  | -3.8 (fixed)           |
| C               | 145258.0022 (67)       |
|                  | $h_{JK} \times 10^4$   |
|                  | 9.6654 (70)            |
|                  | $P_{KKJ} \times 10^5$  |
|                  | 1.59 (37)              |
| $\Delta J$      | 9.29071 (30)           |
|                  | $h_{JK} \times 10^3$   |
|                  | -1.936 (45)            |
|                  | $P_K \times 10^4$      |
|                  | -7.27 (11)             |
| $\Delta JK$     | -45.71991 (99)         |
|                  | $h_K \times 10^3$      |
|                  | 1.1797 (34)            |
|                  | $P_{KKJ} \times 10^7$  |
|                  | -7.21 (27)             |
| $\Delta K$      | 277.4296 (14)          |
|                  | $L_J \times 10^7$      |
|                  | -5.15 (51)             |
|                  | $P_K \times 10^6$      |
|                  | 5.813 (68)             |
| $\delta J$      | 3.689546 (69)          |
|                  | $L_{JJK} \times 10^6$  |
|                  | 4.44 (76)              |
|                  | $p_J \times 10^{10}$   |
|                  | -3.7 (fixed)           |
| $\delta K$      | 10.4168 (26)           |
|                  | $L_{JJK} \times 10^4$  |
|                  | -1.322 (41)            |
|                  | $p_{JJK} \times 10^8$  |
|                  | 2.98 (32)              |
| $H_J \times 10^8$| 1.9494 (68)            |
|                  | $L_{KKJ} \times 10^4$  |
|                  | 5.984 (96)             |
|                  | $P_K \times 10^6$      |
|                  | 1.258 (37)             |
| $H_{JK} \times 10^8$| -7.218 (61)         |
|                  | $L_K \times 10^3$      |
|                  | -3.7138 (70)           |
|                  | $T_K \times 10^8$      |
|                  | -1.229 (33)            |

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