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Analysis of the $\nu_1 + \nu_3$ band of T$_2^{16}$O and the $\nu_1 + \nu_3$ and $2\nu_2 + \nu_3$ bands of DT$_1^{16}$O

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ABSTRACT

We present the $\nu_1 + \nu_3$ band of T$_2^{16}$O and the $\nu_1 + \nu_3$ and $2\nu_2 + \nu_3$ bands of DT$_1^{16}$O that have been analysed for the first time using high-resolution infrared spectra of tritiated water vapour. The spectrum for T$_2^{16}$O has been recorded from a custom-built light-pipe cell at room temperature using a Bruker 125HR Fourier-transform spectrometer at a resolution of 0.025 cm$^{-1}$. For the DT$_1^{16}$O species, an optimised version of the optical cell with 10 times larger maximum activity with regard to previous studies has been employed. For the $\nu_1 + \nu_3$ band of T$_2^{16}$O, we report 206 new experimental line positions in the range from 4415 to 4645 cm$^{-1}$. In the range of 4780–5175 cm$^{-1}$, 356 new experimental line positions of the DT$_1^{16}$O have been assigned for the $\nu_1 + \nu_3$ band and 161 line positions for the $2\nu_2 + \nu_3$ band. The analysis agrees with previous observations showing a systematic shift of the individual line positions compared to the variationally calculated line positions from the Tomsk database. This shift is depending on the rotational quantum number $K_a$. For each band, the assigned lines were used to determine the spectroscopic constants of the $A$-reduced Watson-type Hamiltonian.

1. Introduction

Water is the simplest non-linear molecule and thus it is an interesting test object for molecular quantum mechanics. Spectroscopy of water vapour is mostly motivated by its atmospheric or biological relevance leading to an extensive spectroscopic data set for the non-radioactive isotopologues H$_2$O and HDO, as documented in the HITRAN (High Resolution Transmission) database [1]. For the tritiated water molecules, very little data have been acquired [2–10] prior to efforts by our group.

The theoretical community profits from an extension of the data set with high-resolution spectra from heavy isotopologues HTO, DTO and T$_2$O as it could help to

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understand the breakdown of the Born–Oppenheimer approximation (BO) [11,12]. An extensive and accurate spectroscopic database for radioactive water isotopologues is a prerequisite for designing laser-based analytics in thermonuclear fusion reactors [13,14].

In this work, we present the \( v_1 + v_3 \) band of \( T_2^{16}O \) as obtained in a high-resolution water vapour spectrum from earlier work [15–17]. The isotopic composition of the sample employed back then is dominated by water molecules with protium, H (≈ 90%). Consequently, an improved sample preparation procedure and a new version of the optical cell with a ten times larger maximum activity (10 GBq instead of 1 GBq) has been developed to reveal new, hitherto inaccessible spectroscopic data of DT\(^{16}O\) and \( T_2^{16}O \) due to vanishing signal-to-noise ratio of respective lines. In this paper, we present a first analysis of this spectrum, specifically the \( v_1 + v_3 \) and \( 2v_2 + v_3 \) bands of DT\(^{18}O\).

For the DTO and the \( T_2^O \) bands, we present line lists, a comparison to variational calculations, and spectroscopic constants for the A-reduced Watson-type Hamiltonian.

## 2. Experiment

### 2.1. Experimental setup and procedure

All data have been recorded by a Fourier-transform spectrometer Bruker IFS 125HR applying a resolution of 0.025 cm\(^{-1}\). The absorption spectra for the \( v_1 + v_3 \) \( T_2^{16}O \) band and of the \( v_1 + v_3 \) and \( 2v_2 + v_3 \) DT\(^{16}O\) bands originate from two separate measurements of different samples.

For ensuring a near-nominal instrumental line shape, the alignment status of the FTIR spectrometer is regularly checked by performing gas cell measurements. The cells are filled with HCl, \( C_2H_2 \), or \( N_2O \) [18,19]. The resulting spectra are analysed using the LINEFIT software [20].

For the analysis of the \( v_1 + v_3 \) \( T_2^{16}O \) band, the absorption spectrum acquired in our earlier work has been used [17]. This spectrum has been recorded using a special custom-built spectroscopic cell [21]. Being restricted to a total activity of 1 GBq, this cell has been developed for dealing with the spectroscopic challenges of very small amount of gases while also fulfilling the requirements regarding the materials to avoid degradation due to radio-chemistry. The spectroscopic cell contains the target gases HT\(^{18}O\), DT\(^{18}O\) and \( T_2^{18}O \), as well as \( H_2^{18}O\), HD\(^{18}O\) and \( D_2^{18}O\), \( C^{18}O_2 \) for calibration purposes and traces of methane resulting from reactions of the contained gases with the carbon in the steel. The acquisition was performed by integrating 2358 scans of a duration of 30 s each. The evaluated range of the spectrum extends from 4415 to 4645 cm\(^{-1}\).

The measurement of the \( v_1 + v_3 \) and \( 2v_2 + v_3 \) bands of DTO has been performed with an optimised version of the optical cell. The optimisations are (i) changing of light-guiding pipe from aluminium to the higher-reflectivity silver, (ii) more extensive cleaning cycles before filling, (iii) optimising the geometry, layout and operational parameters of the CuO-reactor that is employed to oxidise the molecular hydrogen isotopologue mixture to tritiated water vapour, and (iv) increasing the total activity to 10 GBq by making use of a special license. These changes result in major improvements in the SNR and the sample purity. While the SNR for HTO remains comparable to that of the previous sample it could be increased by a factor of 5 for \( T_2^O \) and by a factor of 20 for DTO. The total pressure inside of the optical cell has been reduced from a 100 mbar level to a 35 mbar level containing all mentioned residual gases in the previous sample. The composition of the hydrogen isotopes has been shifted from protium as most abundant (≈ 90%) in the former sample to almost equal composition of H:D:T (33%:36%:31%). For the acquisition, an integration of 588 scans, about 30 s long, has been performed. The overlapping \( v_1 + v_3 \) and \( 2v_2 + v_3 \) bands of DTO range from 4780 to 5175 cm\(^{-1}\).

### 2.2. Wavenumber axis calibration

Although the FTIR spectrometer uses a HeNe reference laser, contributions like the finite field-of-view accepted by the interferometer, a minimal misalignment of the FTIR beam path as well as dispersion effects between the HeNe reference laser wavelength and the infrared region makes a calibration of the wavenumber axis mandatory. The calibration has been performed for both spectra separately comparing the absorption lines of residual CO\(_2\) inside the sample with the HITRAN database. For the \( T_2^O \) spectrum 60 lines and for the DTO spectra 20 lines from residual CO\(_2\) have been taken into account. The uncertainties on the line positions of the references lines range according to the HITRAN database from 10\(^{-3}\) to 10\(^{-4}\) cm\(^{-1}\) and are thereby the dominant element of uncertainty of the calibration. Contributions to the uncertainty due to the fitting process, the uncertainties on the pressure shift and the air-broadening parameter have been considered but can be neglected. For the line positions, all sources of uncertainty are taken into account by considering a systematic uncertainty of \( 5 \times 10^{-4} \) cm\(^{-1}\) from the calibration in addition to the individual uncertainties of each line position.
2.3. Line assignments

For the line assignment, the measured spectrum is divided into slices typically of size between 1 and 5 cm$^{-1}$ containing up to 10 lines of the target gases HT$^{16}$O, DT$^{16}$O and T$^{16}$O. A synthetic spectrum is generated for each spectrum slice taking into account the convolution of the Voigt profiles of the interfering lines and the response function of the FTIR spectrograph. Line parameters from interfering lines of non-tritiated gases are obtained from the HITRAN database. Line positions and (relative) intensities for the tritiated water isotopologues have been taken from the Tomsk database [22] and calculated with the variational approach from the potential energy surface of Partridge and Schwenke [23]. Although the observed line positions deviate from these theoretical predictions by up to ±0.3 cm$^{-1}$, the accuracy of the relative line intensities and the relative distance of lines within a band permits to perform an initial visual assignment.

With the robust minimisation algorithm MINUIT [24] via the iminuit$^1$ Python library, parameters of the synthetic spectrum have been determined including the line intensities and line centres here presented with their individual uncertainties. We confirmed via a Monte-Carlo study with simulated blending spectral lines that these fit uncertainties represent the actual uncertainty. To exclude any wrong assignment during the initial visual assignment, all line positions have been tested for plausibility by fitting the line list to the effective molecular Watson-type Hamiltonian as discussed below.

3. Results and discussion

3.1. Experimental line list and spectra

We present 206 lines of the $\nu_1 + \nu_3$ band of T$^{16}$O, 356 of the $\nu_1 + \nu_3$ band of DT$^{16}$O and 161 lines of the $2\nu_2 + \nu_3$ band of DT$^{16}$O with rotational quantum numbers up to $J' = 16$ and $K'_a = 8$. These bands have been analysed for the first time. Each line of the total 723 lines has an individual statistical uncertainty from the fitting procedure in a range of $4.3 \times 10^{-4}$ cm$^{-1}$ to $4.0 \times 10^{-2}$ cm$^{-1}$.

Both DTO bands are subject to frequent blending by

![Figure 1](image-url). The assigned lines for each band (coloured) are compared in line intensity and position to the variational calculations from the Tomsk database (http://spectra.iao.ru) [22] (black). The relative line intensities between the bands are indicated by the absolute value in arbitrary units. The colour represents the order of magnitude of individual line uncertainty. The contribution to the uncertainty resulting from calibration is not included.
lines of residual gases, leading to overall larger uncertainties for the line positions, intensities and to less assigned lines than expected from improvements by the optical cell.

Figure 1 presents a comparison of the assigned spectral lines of the 3 bands with the variational calculation from the Tomsk database. The individual uncertainty on the line position of each line is colour coded.

![Figure 1](image1.png)

**Figure 2.** Difference of the assigned line positions to the theoretical positions from the Tomsk database for each transition. Markers and colours are indicating the value of the $K'$ quantum number the vertical lines the uncertainty on the line position.
3.2. Comparison of the assigned lines with variational calculations

The lines of the two DTO bands are subject to strong line blending. To achieve the best results for the line positions in the fitting procedure a larger range for the fitting parameters corresponding to the line intensity and the pressure of the sample has been accepted. This leads to some discrepancies in the line intensity between the predictions from the variational calculations and the assigned lines of the two DTO bands. At this point, it should be noted that the larger range of the fitting parameter pressure has no effect on the line positions as a pressure-dependent shift is not included. In Figure 2, the differences between the observed line positions to the ab-initio line positions from the Tomsk database are plotted over the observed line positions including the uncertainties of the line position as error bars for the differences. As shown in previous observations [16,17], the assigned lines are shifted by a band-specific value of up to ±0.3 cm⁻¹ corresponding to over 10 line widths while the distribution within a band around this value is comparably smaller and follows a dependency on quantum numbers. This dependency is most visible in J′ (and J″) as a parabolic shape in the difference to Tomsk database and in K′α (and K″α) indicated in the plot by various colours.

Starting from the fit to non-perturbed Watson Hamiltonian parameters shown in the following paragraph and also taking into account previously assigned bands, the dependence of these discrepancies with quantum numbers cannot be ascribed to resonances. Therefore, we assume that the ab-initio calculation generates small, systematic deviations for the rovibrational energies.

3.3. Fit of the spectroscopic constants for the A-reduced Watson Hamiltonian

To prevent bias from the visual assignment a consistency check is mandatory. For this purpose, the line positions have been used to reproduce the spectroscopic constants of the ground state of the A-reduced Watson Hamiltonian [25] including the line positions of Helinger [3] for the DTO and De Lucia [2] for T₂O obtained by rotational microwave spectrometry. The fits have been performed for each of the three bands separately. Between 91 (DTO 2ν₂ + ν₃) and 590 (DTO ν₁ + ν₃) combinational differences could be formed from all assigned lines which led to an RMS of less than 8.9 × 10⁻³ cm⁻¹. A comparison of all fit parameters with the results of the microwave measurements is given in the supplementary material. This agreement confirms that the line assignments based on variational calculations in the Tomsk database have been performed correctly.

To enable the reproduction of the transitions bands from spectroscopic parameters, the constants of the ground state and the assigned line positions have been used for the fit of the spectroscopic constants in the Watson A-reduced Hamiltonian for the upper state. For each band, the constants given in Table 1 have been obtained with a resulting RMS value of up to 4.7 × 10⁻³ cm⁻¹ for a distortion parameter set of up to octic order. The prediction error of the model agrees with the resulting uncertainties of the fitted line positions. The latter are derived from the noise level of the measured spectrum also taking into account line blending effects. For the DTO bands, only a few lines had to be excluded for the Watson fit. However, for the ν₁ + ν₃ band of T₂O the number of lines

| Parameter | Value 2σ | Value 2σ | Value 2σ |
|-----------|----------|----------|----------|
| A         | 10.8486 (10) | 13.11925 (30) | 15.17958 (50) |
| B         | 4.79309 (56) | 5.651783 (74) | 5.83650 (12) |
| C         | 3.27217 (41) | 3.885394 (57) | 3.853250 (80) |
| 1 × 10³ × ΔK | 0.057 (11) | 0.17476 (90) | 0.2210 (13) |
| 1 × 10³ × ΔK | -1.540 (70) | -0.444 (12) | -0.958 (15) |
| 1 × 10³ × ΔK | 0.0727 (15) | 0.05218 (21) | 0.13040 (64) |
| 1 × 10³ × ΔK | -0.0265 (76) | 0.06418 (32) | 0.08451 (53) |
| 1 × 10³ × δK | 1.52 (16) | 0.3627 (64) | 1.0826 (89) |
| 1 × 10³ × δK | -6.65 (92) | 1.86 (24) | 0.102 (18) |
| 1 × 10³ × δK | -1.86 (15) | 0.958 (15) | 0.510 (60) |
| 1 × 10³ × δK | 10.3 (18) | 0.090 (41) | 0.510 (60) |
| 1 × 10³ × δK | -2.36 (27) | 0.534 (74) | 0.019 (11) |
| 1 × 10³ × δK | 1.233 (99) | 0.00967 (73) | 0.0297 (19) |
| 1 × 10³ × δK | 5.25 (15) | -0.102 (18) | 0.019 (11) |
| 1 × 10³ × δK | -2.56 (87) | 0.090 (41) | 0.510 (60) |
| 1 × 10³ × δK | 2.85 (10) | 0.534 (74) | 0.019 (11) |
| ν₀ | 4544.6705 (18) | 5021.08037 (76) | 4880.80833 (99) |
| RMS | 0.004459 | 0.004475 | 0.004739 |
| No. of fitted lines | 103 | 314 | 148 |
has been reduced to quantum numbers $J \leq 9$ and $K_a \leq 4$ eliminating 50% of the lines. Including lines with large $J$ and $K_a$ led the fit to break down indicating possibly some resonances with nearby vibrational states, or the failure of the employed Hamiltonian expansion.

Consistent with HTO in previous observations [17], we show here that the Watson Hamiltonian is an appropriate representation for DTO and T$_2$O for low $J$ and $K_a$ quantum numbers. However, the breakdown of the Born–Oppenheimer approximation especially for large $K_a$ as discussed in [11,12] limits the application to small $K_a$.

4. Conclusion

After previously assigning six bands of HT$^{16}$O and the $v_1 + v_3$ fundamental band of DT$^{16}$O [15–17], we now present 206 lines of the $v_1 + v_3$ band of T$_2$O$^{16}$O from the same measured spectrum. A dilution by residual protium has been observed shifting the composition of the sample strongly to the HT$^{16}$O as can be noted from the numbers of lines presented from this spectrum. This effect has also been observed in the study of Kobayashi et al. [10,14].

To suppress this effect, the procedure and the optical cell have been improved and a 10 times larger amount of activity has been used. From the spectrum of this improved setup, we present 356 lines of the $v_1 + v_3$ and 161 lines of the $2v_2 + v_3$ band of DT$^{16}$O that have not been available before. The analysis of the composition shows that all hydrogen isotopes are represented almost equally (H:D:T = 33%:36%:31%).

As observed in previous studies, the difference between the measured lines to those in the Tomsk database shows a strong dependency on $K_a$. At the same time, the fits of the lines to the $A$-reduced Watson-type Hamiltonian break down for larger $K_a$, both probably resulting from the breakdown of the Born–Oppenheimer approximation.

Further assignments of the tritiated water species as well as an extension to the tritiated water species with $^{17}$O and $^{18}$O may give opportunity to the theoretical community to investigate the adiabatic and non-adiabatic contributions of one of life’s most important molecules.

Note

1. https://github.com/scikit-hep/iminuit.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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