

Absorption spectra of HDO and HTO in near IR spectral range

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Abstract

Different processes of nuclear fuel cycle are followed by release of deuterium – D and tritium – T. Their isotope exchange with hydrogen in atmosphere water vapour leads to HDO and HTO molecules presence in air. Hence, presence of these water isotopomers above their concentration in normal atmosphere near facility under inspection is signature of nuclear activity. D is stable isotope, its natural abundance is $1.5 \cdot 10^{-4}$ (for example see [1]). T is unstable isotope with decay time - 12.33 years. Its concentration in atmosphere is very low because main source of T generation in atmosphere is due to space neutrons (each minute ~ 10 atoms/cm²).

All water isotopomers under consideration (H₂O, HDO, HTO) have absorption in near IR (overtone of H-O bond) and can be detected by TDLS with high sensitivity. H₂O spectra were investigated recently with very high sensitivity [2], while HDO spectra were obtained only for natural abundance. Up to authors knowledge there is no information about HTO in this spectral range.

In present paper results of HDO and HTO spectra investigation using TDLS technique are presented. Two samples were investigated: normal water and heavy water containing T (H:D = 0.57, T:D = 0.01). Lines observed in H₂O spectrum were in agreement with [1]. For heavy isotopomers we observed several disagreements demonstrating wrong lines identification for HDO and presence of additional lines with respect to [1]. Future spectra analysis is in progress.

Heavy water

Natural abundance of different water isotopomers.

Molecule	[1]
H ₂ ¹⁶ O	0.997317
H ₂ ¹⁸ O	1.99983E-03
H ₂ ¹⁷ O	3.71884E-04
HD ¹⁶ O	3.10693E-04
HD ¹⁸ O	6.230E-07
HD ¹⁷ O	1.158E-07
D ₂ ¹⁶ O	2.41E-08

There is a number of effective methods of heavy water production: electrolysis, isotopic exchange and incineration of hydrogen enriched by deuterium. Today heavy water is produced by thousands of tons. The major property of heavy water is that it practically do not absorbs neutrons. That is why it is using in nuclear reactors (modern reactor needs 100-200 tons of heavy water with purity not less than 99,8%).

Near facility D will be presented in form of HDO molecule.

References:

[1] L.S. Rothman, et.al, The HITRAN 2004 molecular spectroscopic database, 96, pp. 139-204 (2005); J.Phys.Chem.Ref.Data, 13, 809-891 (1984)

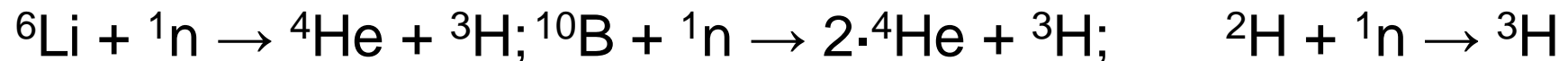
[2] R.Toth, Linelists of water vapor parameters from 500 to 8000 cm⁻¹, <http://mark4sun.jpl.nasa.gov>

Super-heavy water

Tritium (${}^3\text{H} = \text{T}$) – is radioactive super-heavy hydrogen radionuclide with mass number 3. Tritium has β decay with half-time 12,33 year. β particles has energy $< 18,6$ keV and free path length in atmosphere ~ 1 mm. Natural tritium forms at bombardment of nitrogen by cosmic radiation neutrons:



Similar reaction can take place also with neutrons from nuclear reactor. In nuclear reactors tritium is producing due to following reactions:



Consequently, tritium escapes from different nuclear fuel processes and from used fuel elements and can be signature of un-legal nuclear activity. In atmosphere tritium will be presented in form of HTO molecule.

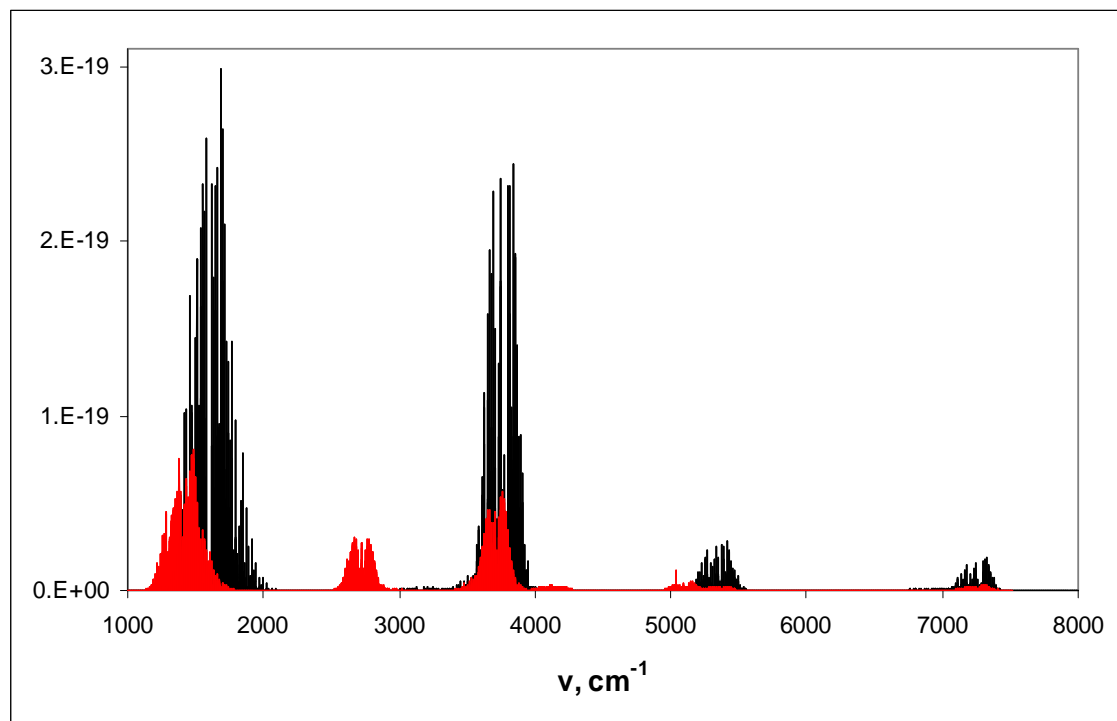
Tritium concentration estimation

Tritium is the main radioactive component of liquid chops and gaseous outbursts of most nuclear power stations, since it practically remains unaffected by filtration. It leads to pollution of soil, subterranean and superficial water around facilities. It was shown long ago, that in vicinity of some American nuclear power stations NPS content of tritium in needles of trees on windward side was 10 times as much as on leeward side – direct proof that exactly station is the source of tritium.

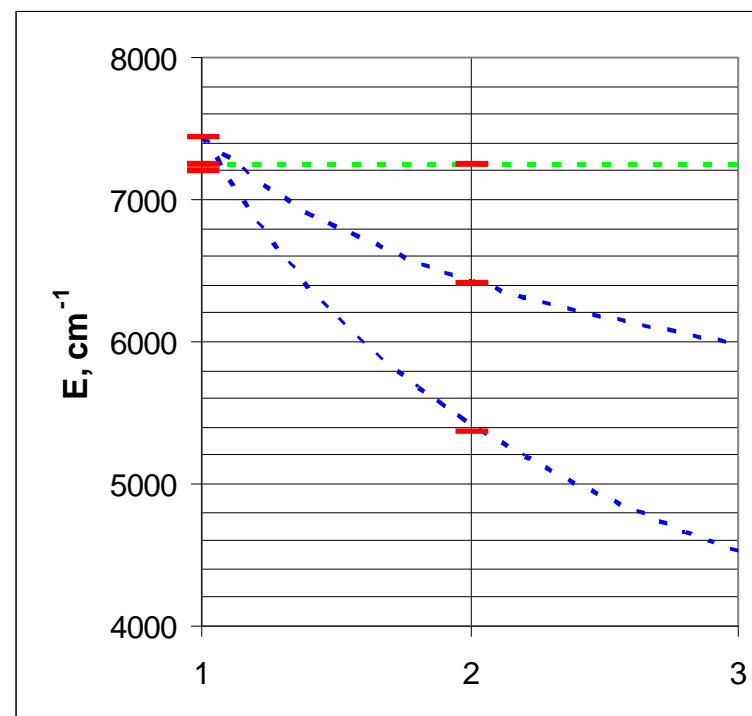
Natural concentration of HTO in water is at 10^{-18} level. In vicinity of processing plants (according to some data available about tritium ejection in atmosphere) tritium concentration rough estimation is 0.1 – 1.0 ppb.

Water absorption spectra

H₂O spectra were investigated recently with very high sensitivity [2], while HDO spectra were obtained only for natural abundance. Up to authors knowledge there is no information about HTO in this spectral range.



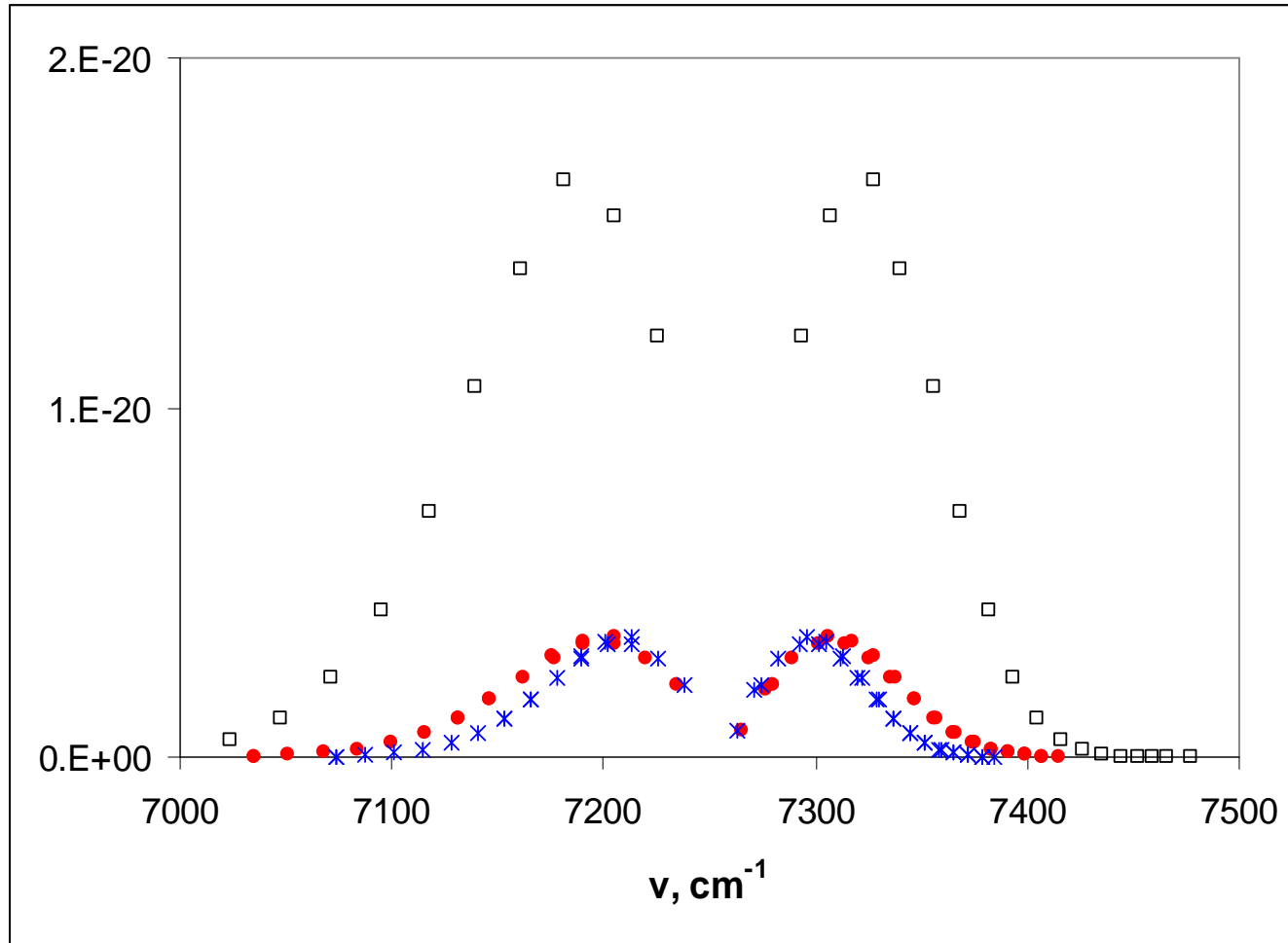
Spectra of H₂O (black) and HDO (red).



Isotope shift (H₂O, HDO, HTO) of H-O bond overtone [1].

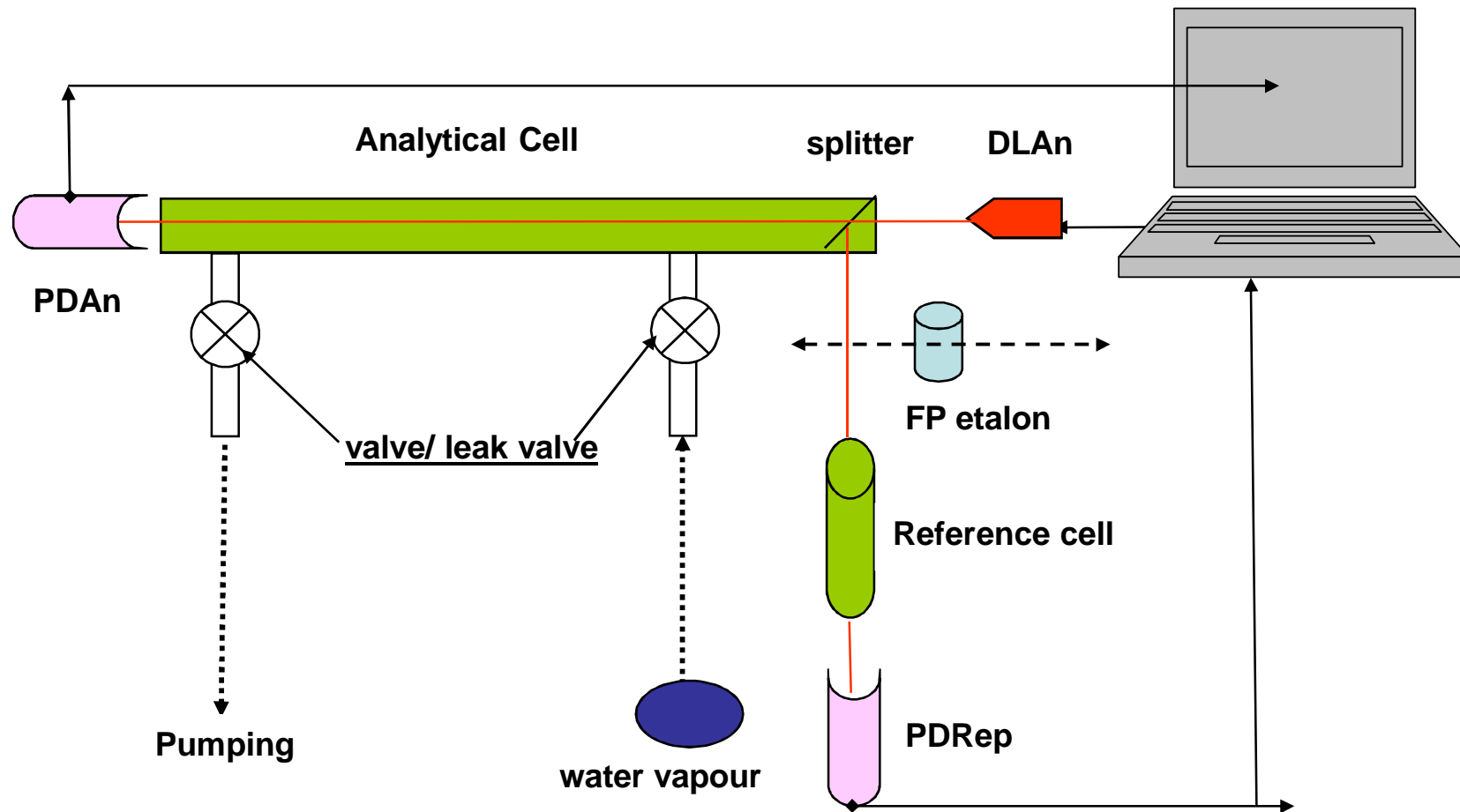
All water isotopomers (H₂O, HDO, HTO) have absorption in near IR (overtone of H-O bond) and can be detected by TDLS with high sensitivity.

Water absorption spectra in near IR



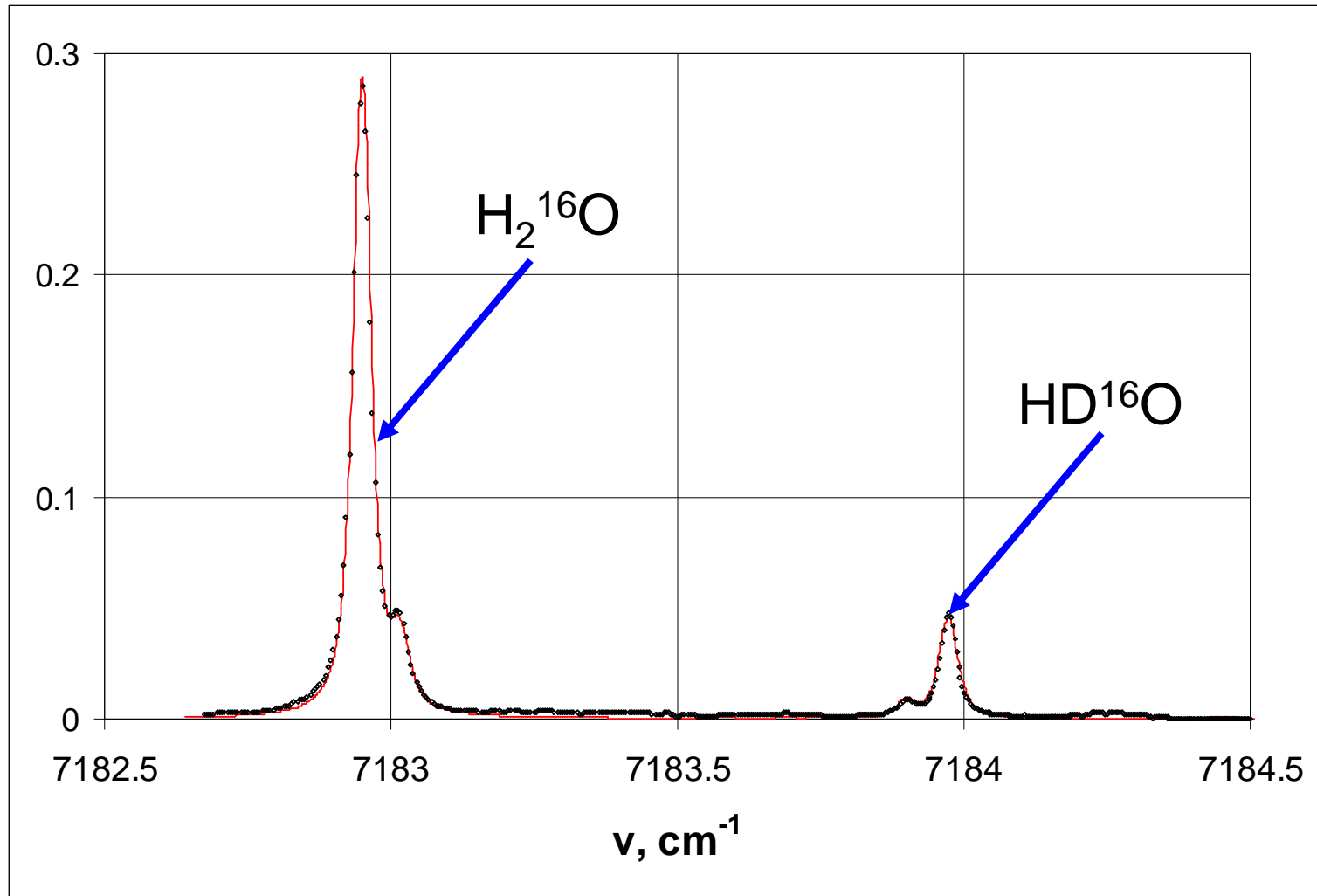
Absorption spectra (each point corresponds to most intensive line in rotation manifold) for H_2O (black) and HDO (red) [1]. Based on these data and analysis performed model of HTO absorption spectrum was developed (blue).

Block-scheme



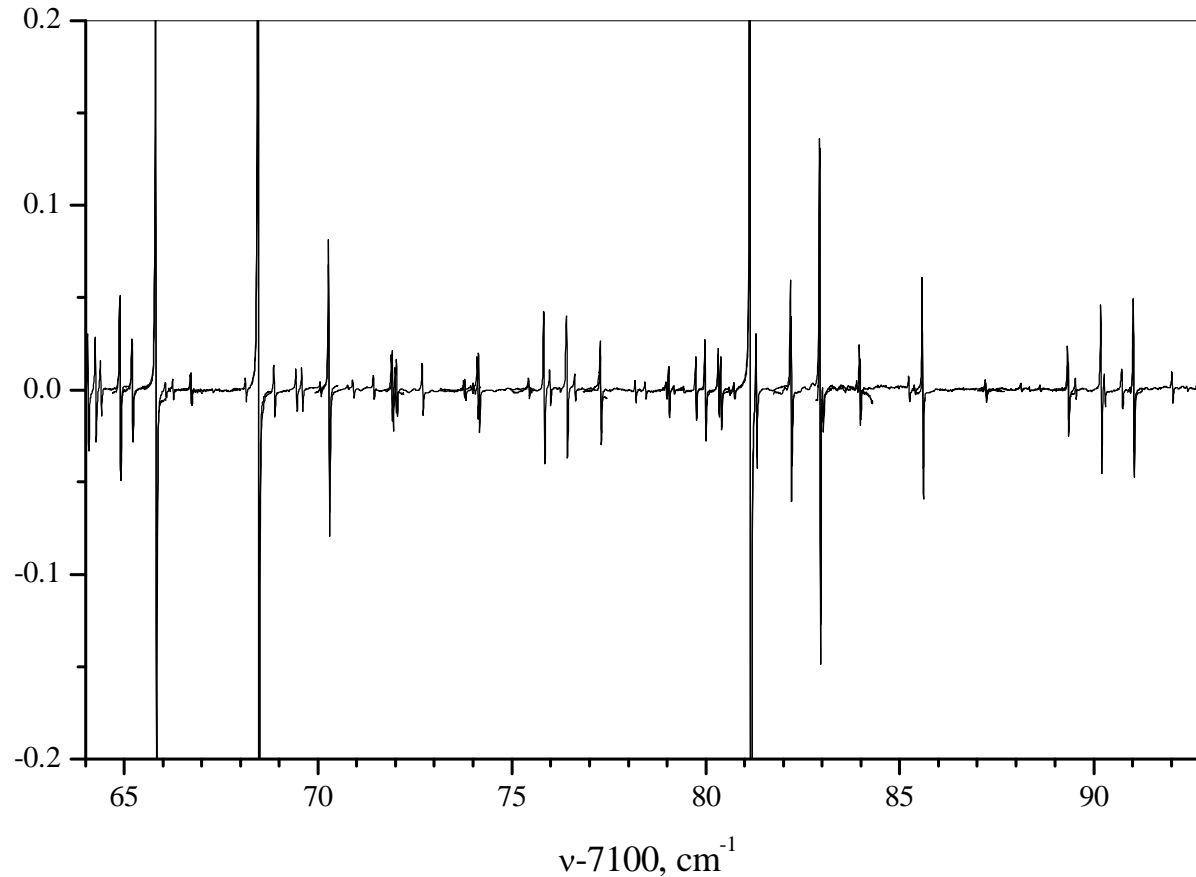
Two channels DL spectrometer: one channel with FP etalon (0.0497 cm^{-1}) or reference cell was used to determine DL frequency tuning curve. Analytical channel contains sample cell ($L=12$ or 100 cm). DFB DL (Laser Components) operated near 1.39μ where water isotopomers absorption bands are located.

Water spectrum fragment



Fragment of recorded water vapor absorption spectrum (black points) and its fitting (red line) for one of investigated heavy water sample

Water spectrum



Spectra of two water samples were obtained in present work.

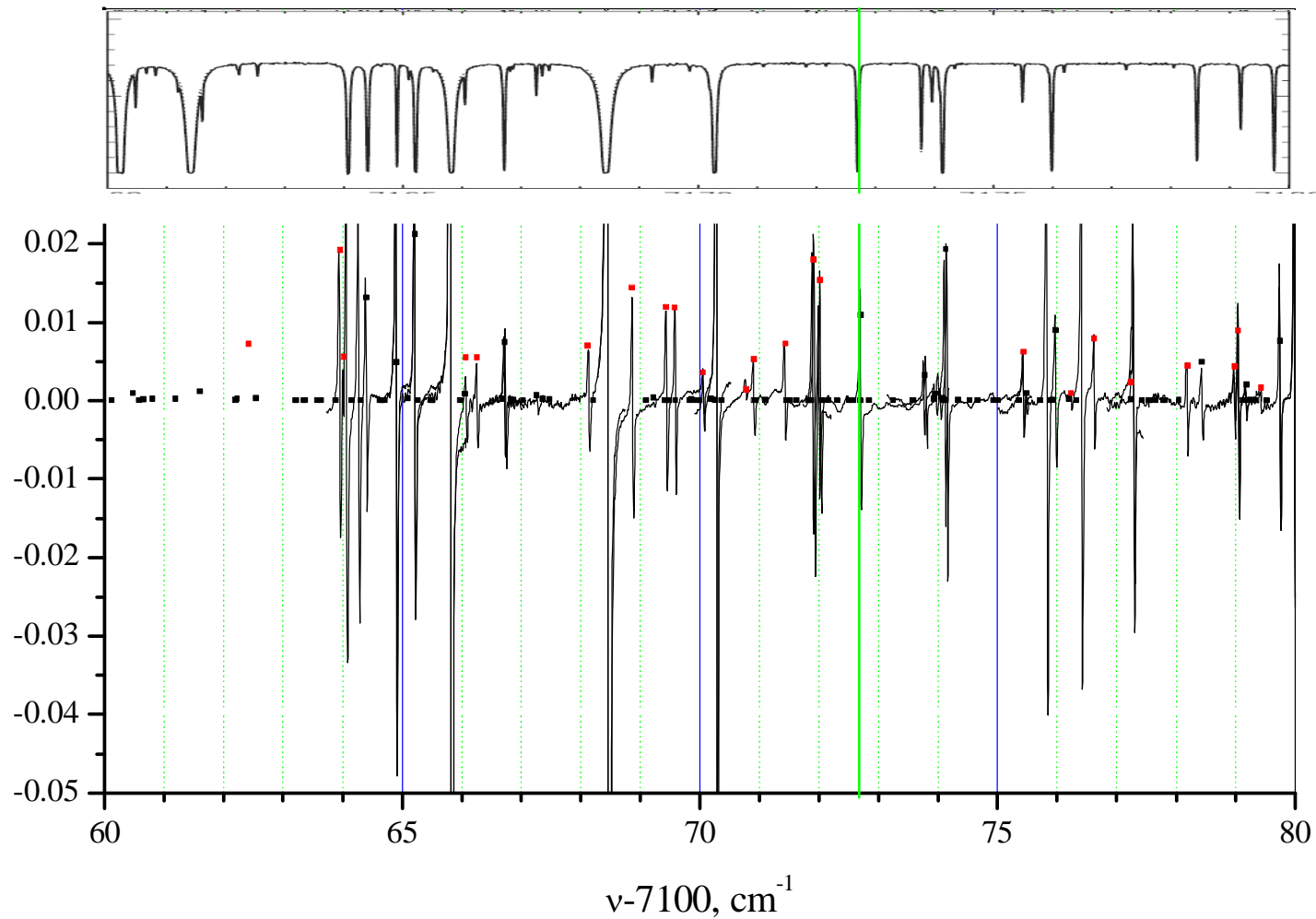
Sample #1 - natural isotopes abundance.

Sample #2 - H:D = 0.57, T:D = 0.01.

Pressure in analytical cell was 5-10 Torr.

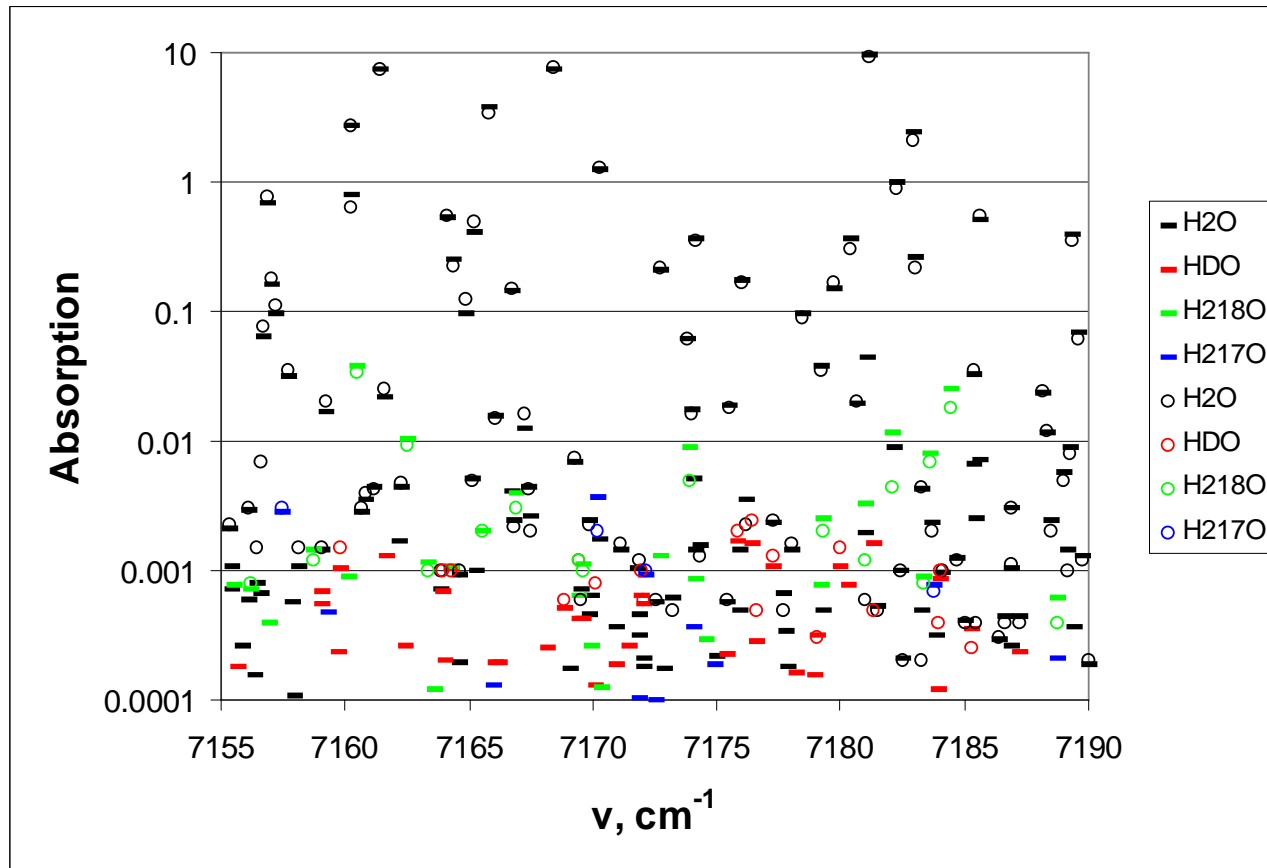
Differential spectrum of sample #2. This spectrum consists of 18 fragments recorded at different DL temperatures. Each fragment was obtained using DL frequency tuning by excitation current; frequency was calibrated with help of FP etalon and known frequency of one of water lines.

Lines identification



Recorded spectral lines were identified based on [2]

Sample #1 spectrum



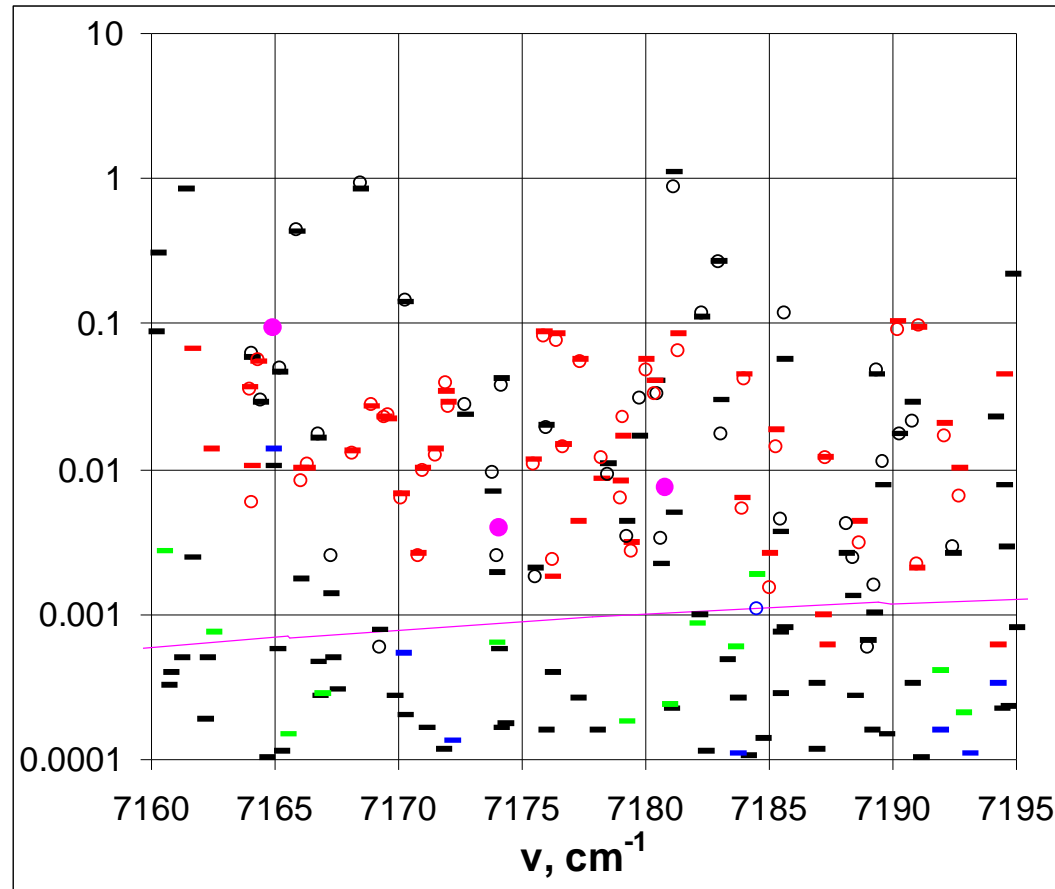
Sample #1 - natural isotopes abundance; L=12, 100 cm. Spectrum was obtained in spectral range 7155-7192 cm^{-1} .

Lines statistics

Total	143
H ₂ ¹⁶ O	98
HD ¹⁶ O	20
H ₂ ¹⁸ O	19
H ₂ ¹⁷ O	6
Non-identified	0

143 lines were recorded (cycles) in this spectral range having absorption between 0.0001 and 10. All these lines were identified as belonging to 4 water isotopomers (dashes).

Sample #2 spectrum



Sample #2 - H:D = 0.57,
T:D = 0.01; L=12 cm.
Spectrum was obtained
in spectral range 7164-
7193 cm⁻¹.

78 lines were recorded (cycles) in this spectral range having absorption between 0.001 and 1. 75 lines were identified as belonging to 3 water isotopomers (dashes). 3 lines not included in [2] were recorded being far above solid curve (HTO model).

Lines statistics

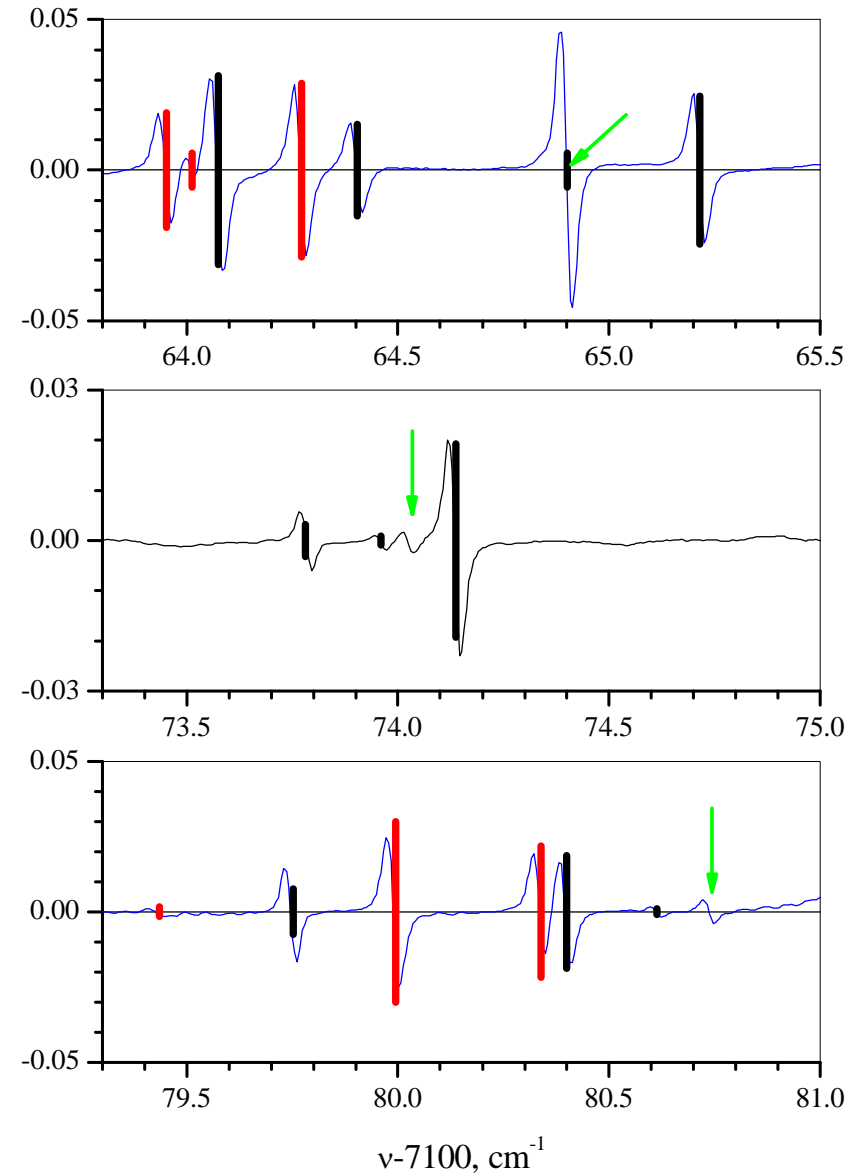
Total	78
H ₂ ¹⁶ O	35
HD ¹⁶ O	39
H ₂ ¹⁸ O	1
H ₂ ¹⁷ O	0
Non-identified	3

Non-identified lines

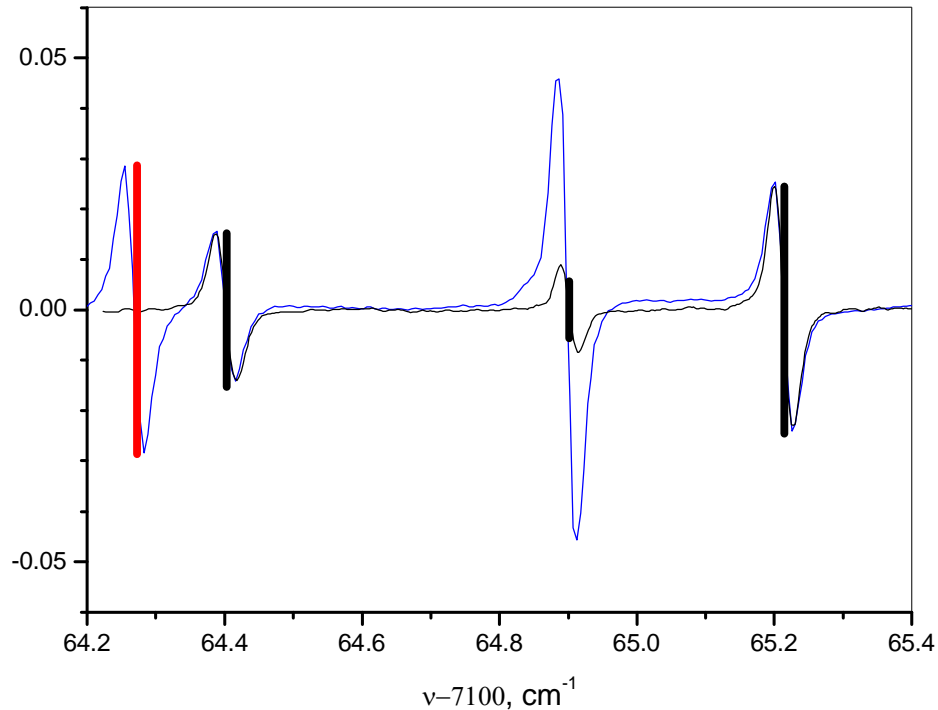
Three spectral ranges containing non-identified lines. Blue curve sample #2 spectrum. Black and red vertical lines correspond to line positions and intensities ([2] and the sample isotope abundance) for H_2^{16}O and HD^{16}O , respectively.

For lines majority more or less good agreement can be observed between our experiment and [2].

Non-identified lines are shown by green arrow.



Conclusion



Normalized spectra of sample #1 (black) and #2 (blue). The spectra were normalized to have the same absorption for H_2O lines. The figure explains the above mentioned problem.

There is overlapping of H_2O and HDO lines. This overlapping leads to wrong HDO lines identification in [2]. It is known that wrong identification results in predicted lines disappearing and presence of un predicted lines.

Observed lines can not belong to HTO. Further investigation is necessary: both theoretical one with correct line assignment and more sensitive spectra recording.