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HTO detection using TDLS

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DLS LAB

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Introduction

Reactors with heavy water

$$D_2O,\ DTO$$

Heavy water leakage to atmosphere due to isotope exchange with atmosphere water

$$D_2O,\ DTO + H_2O \Rightarrow HDO,\ HTO$$

Neutrons interaction with atmosphere water

$$n + H_2O \Rightarrow HDO$$
$$n + HDO \Rightarrow HTO$$

Objective: using TDLS detect increase of HDO concentration and HTO presence

Heavy water

Natural abundance of different water isotopomers.

Molecule	[1, 2]
$H_2{}^{16}O$	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] HITRAN (v11.0), http://cfa-www.harvard.edu/hitran
[2] L.S. Rothman, D. Jacquemart, A. Barbe, D. Chris Benner, M. Birk, L.R. Brown, M.R. Carleer, C. Chackerian Jr., K. Chance, L.H. Coudert, V. Dana, V.M. Devi, J.-M. Flaud, R.R. Gamache, A. Goldman, J.-M. Hartmann, K.W. Jucks, A.G. Maki, J.-Y. Mandin, S.T. Massie, J. Orphal, A. Perrin, C.P. Rinsland, M.A.H. Smith, J. Tennyson, R.N. Tolchenov, R.A. Toth, J. Vander Auwera, P. Varanasi, G. Wagner, The HITRAN 2004 molecular spectroscopic database, Journal of Quantitative Spectroscopy and Radiative Transfer, vol. 96, pp. 139-204 (2005)

Super-heavy water

Tritium (^3H = 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 ~ 1mm. Natural tritium forms at bombardment of nitrogen by cosmic radiation neutrons:

$$^{14}N + {}^1n = {}^3H + 4\cdot{}^4He \text{ (each minute} \sim 10 \text{ atoms/cm}^2).$$

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

$$^6Li + {}^1n \rightarrow {}^4He + {}^3H; \quad ^{10}B + {}^1n \rightarrow 2\cdot{}^4He + {}^3H; \quad {}^2H + {}^1n \rightarrow {}^3H$$

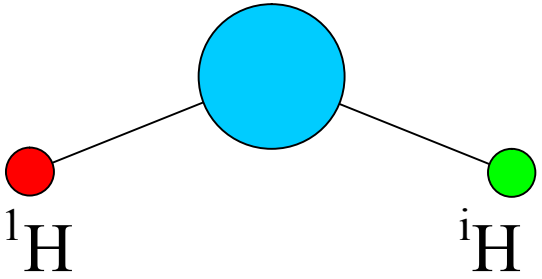
Consequently, tritium escapes from different nuclear fuel processes and from used fuel elements and can be signature of un-legal nuclear activity. ***In atmosphere tritium will be presented in form of HTO molecule.***

Water spectroscopy (references)

H_2O spectra were investigated recently with very high sensitivity [3], while HDO spectra were obtained only for natural abundance. For HTO there are only 4 papers [4-7]. Experimental spectra of v_2 [4] and v_1 [6] bands and their theoretical analysis [6, 7]. Up to authors knowledge there is no information about v_3 band. Paper [5] is related to trace HTO detection.

References:
[3] R.Toth, Linelists of water vapor parameters from 500 to 8000 cm-1, ttp://mark4sun.jpl.nasa.gov
[4] P. P. Cherrier, P. H. Beckwith and J. Reid, Linewidths and linestrengths in the v2 band of HTO as measured with a tunable diode laser, *JMS, 121, 69-74 (1987)*
[5] Pierre P. Cherrier and John Reid, High-sensitivity detection of tritiated water vapour using tunable diode lasers, Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment, Volume 257, 412-416 (1987)
[6] S. D. Cope, D. K. Russell, H. A. Fry, L. H. Jones and J. E. Barefield, Analysis of the v_1 fundamental mode of HTO, JMS, 127, 464-471 (1988)
[7] O. N. Ulenikov, V. N. Cherepanov and A. B. Malikova, On analysis of the v_2 band of the HTO molecule, JMS, 146, 97-103 (1991)

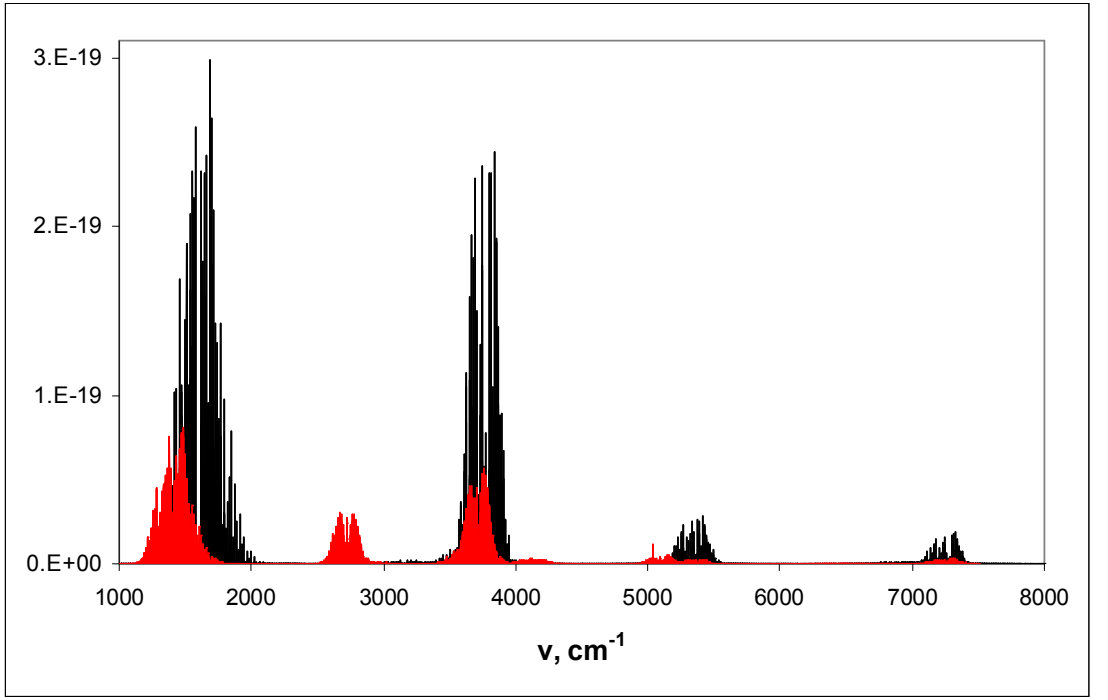
Water molecule vibration modes



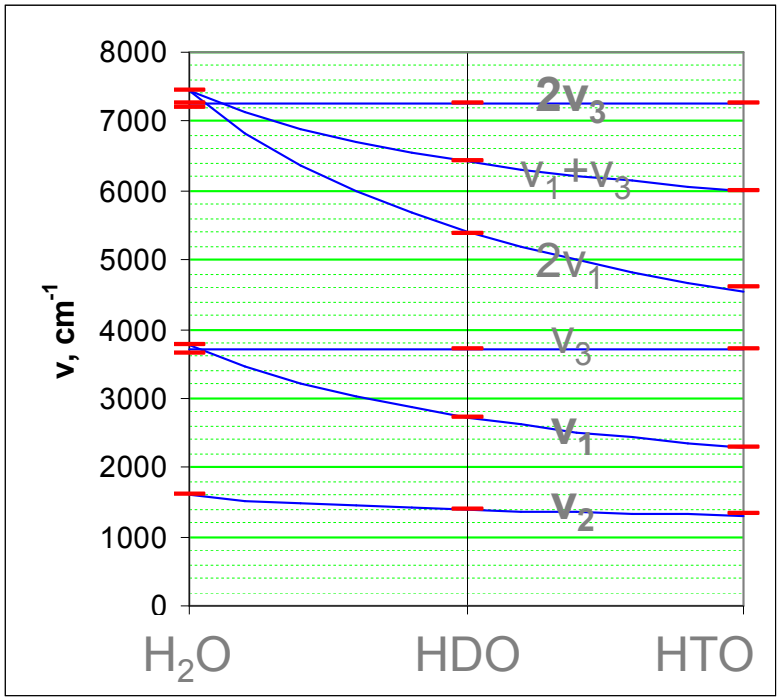
^{1}H = H

^{2}H = D

^{3}H = T



Spectra of H_2O (black) and HDO (red).



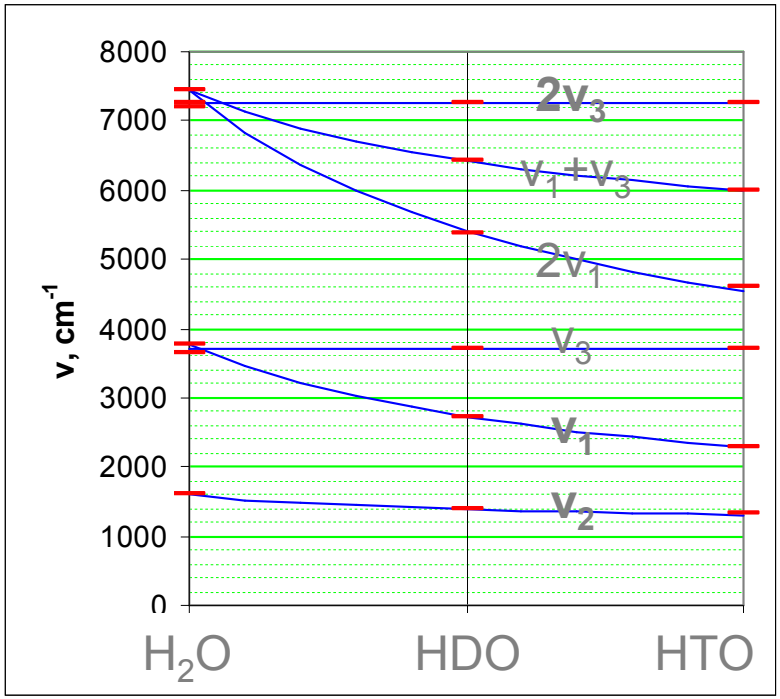
Isotope shifts of water vapour bands (H_2O, HDO, HTO).

v_1 – (O)-(^{i}H) stretching vibration

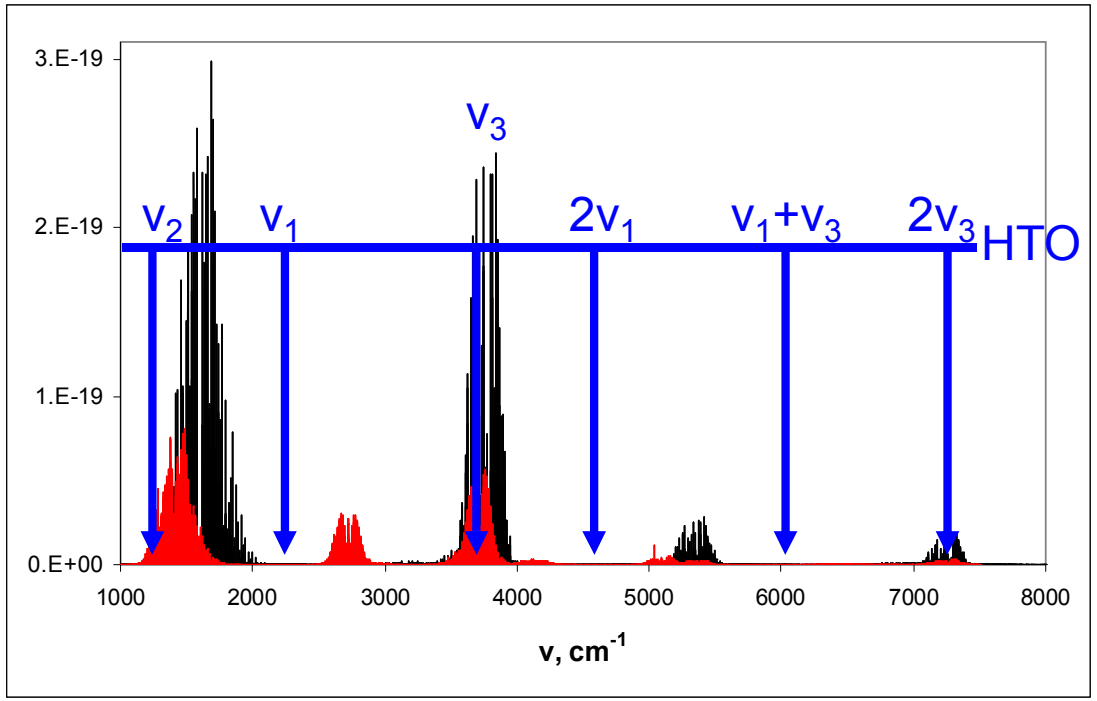
v_2 – bending vibration

v_3 – (O)-(H) stretching vibration

Spectral ranges for HTO detection



Isotope shifts of water vapour bands (H_2O, HDO, HTO).



Spectra of H_2O (black) and HDO (red). Blue - HTO bands.

HTO absorption bands:

v_2 – possible. The same spectral range as for UF_6 enrichment measurement.

v_1 – possible.

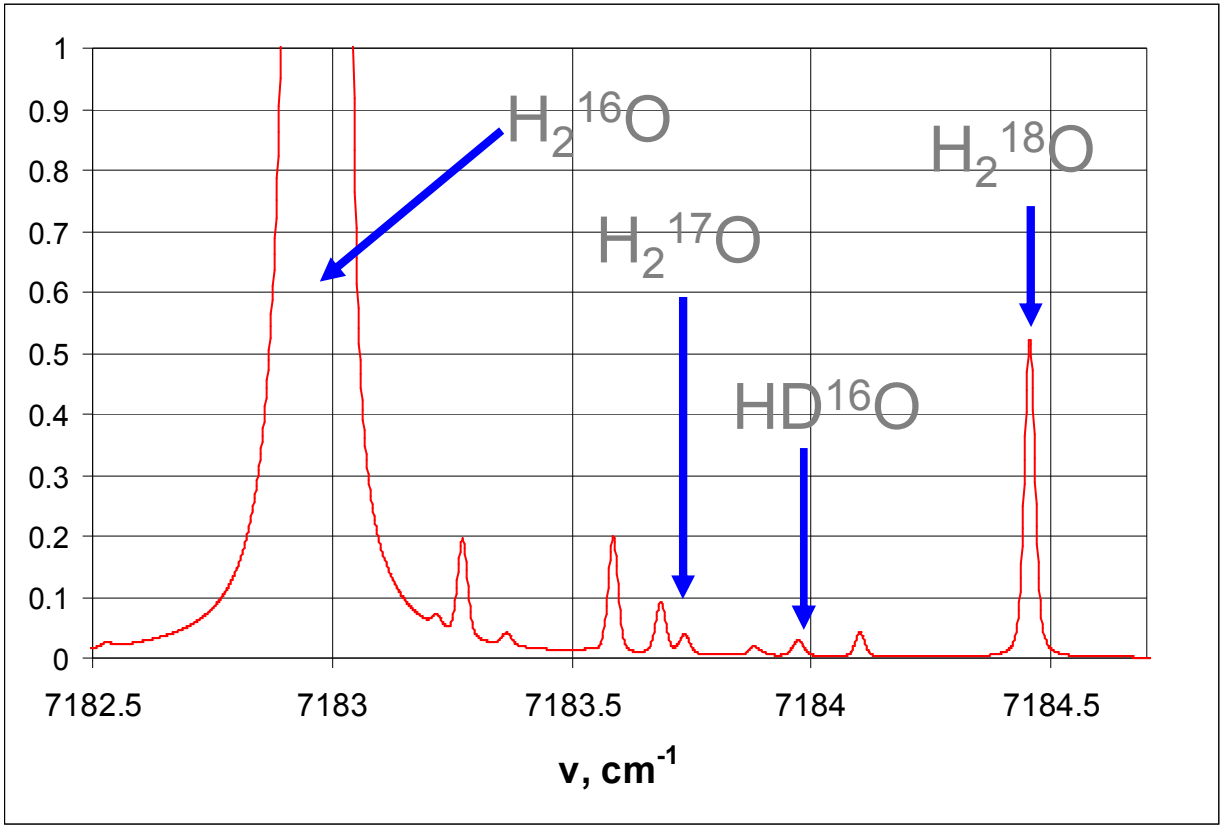
v_3 – No advantage with respect to $2v_3$.

$2v_1$ – possible.

v_1+v_3 – Too weak, no advantage with respect to $2v_3$.

$2v_3$ – possible. Below we'll consider possibility of HTO detection in this band.

Advantage and disadvantage of $2\nu_3$



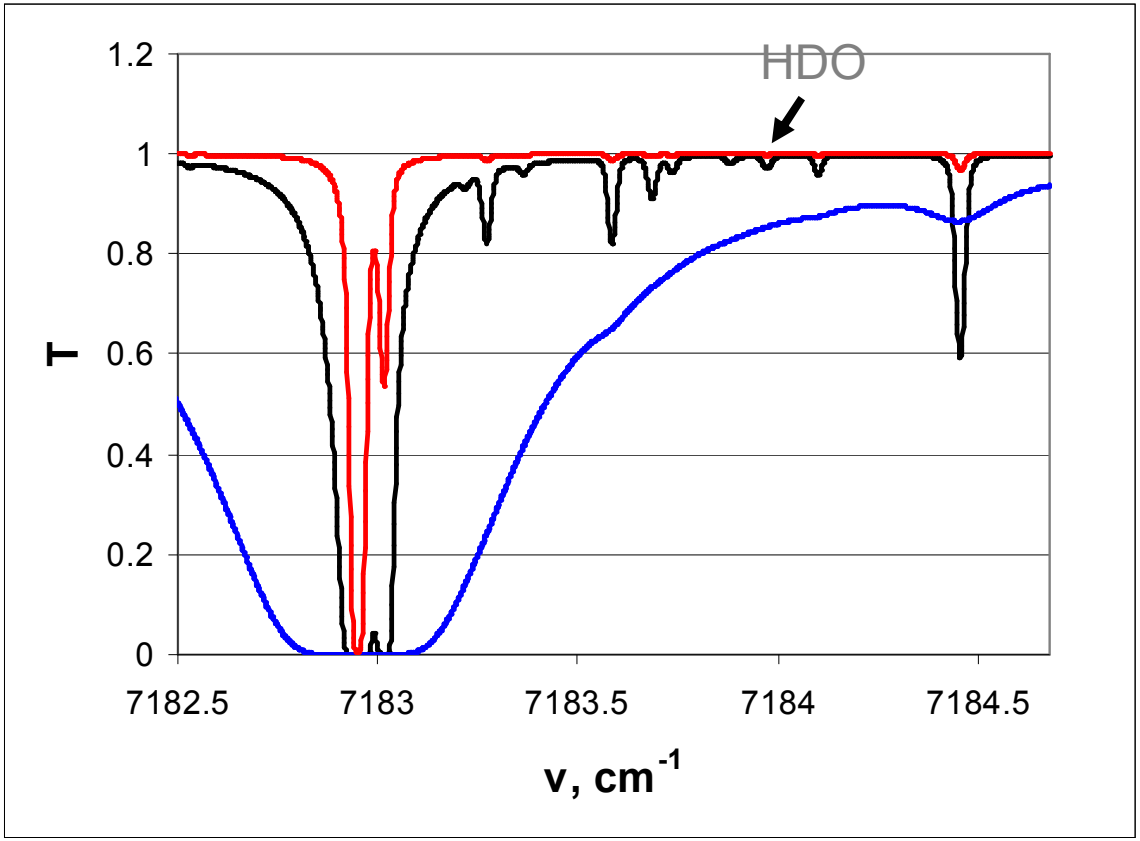
Absorbance spectrum of water vapor with natural isotopes abundance:

L = 39 m, P = 5 Torr

Advantages:

1. It is possible to measure all hydrogen and oxygen isotopes in the same spectral range.
2. DL are commercially available, reliable, and not very expensive.

Advantage and disadvantage of $2v_3$



Transmission spectra of water vapor with natural isotopes abundance (L = 39 m):

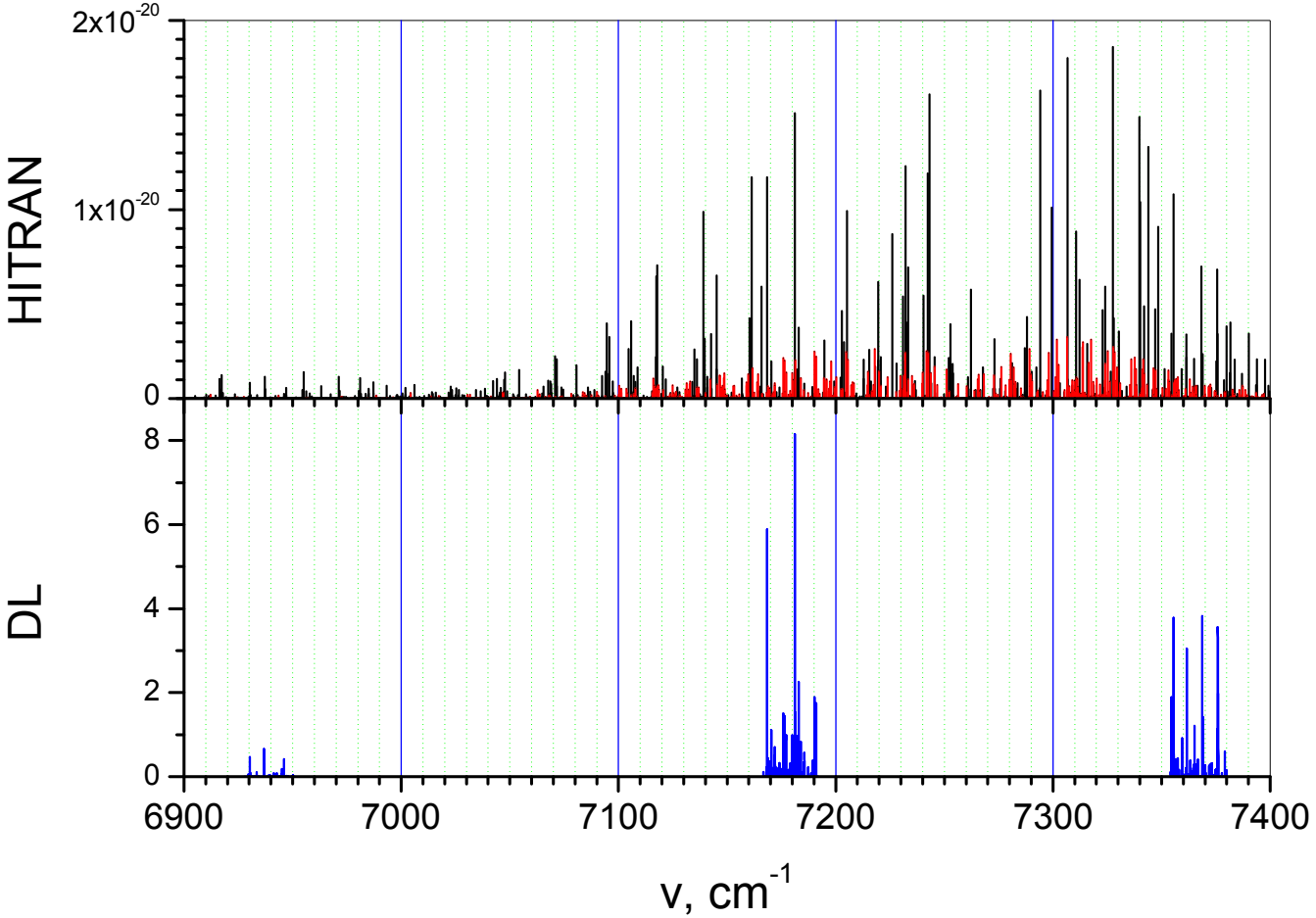
Black: Water vapor with P_{H2O} = 5 Torr (the same as on previous slide) .

Blue: Atmosphere air, P_0 = 760 Torr, 50 % of humidity.

Red: The same as above, P_0 = 30 Torr.

Disadvantage: it is necessary to measure trace absorption in presence of strong water lines. It needs low pressures. To increase sensitivity sample enrichment is required (similar to UF_6 gas handling system).
$2v_1$ (around 4600 cm^{-1}) is free of these disadvantage and can be considered as alternative even in case of worse sensitivity.

$2v_3$ water spectra



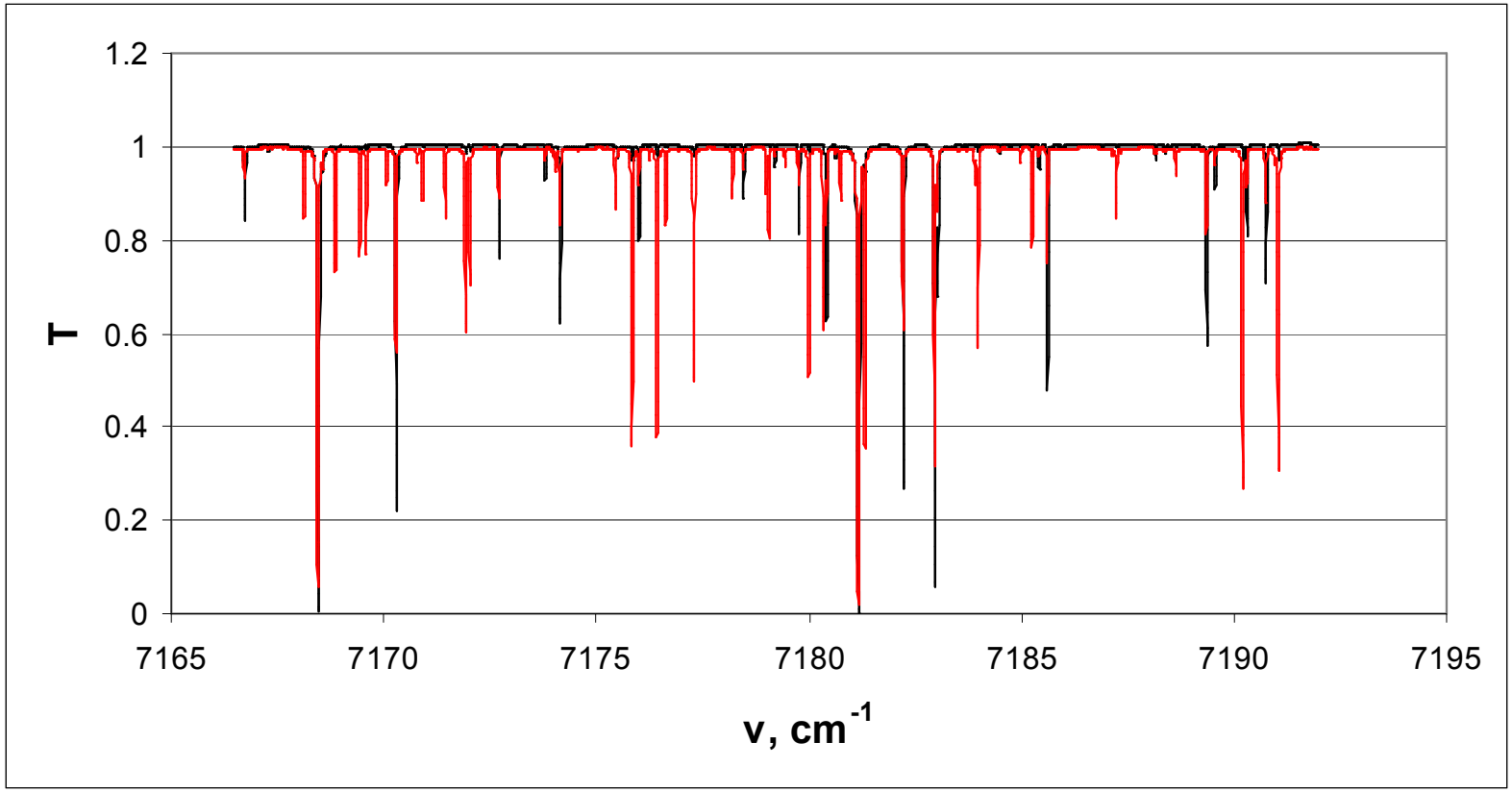
HITRAN spectra of H_2O (black) and HDO (red)

Water samples spectra were recorded using 3 Diode Lasers (blue) operated at 1.44, 1.39, and 1.36 μ

Analysis of water vapor spectra near 1.39 μ are presented in present paper.

TDLS spectra

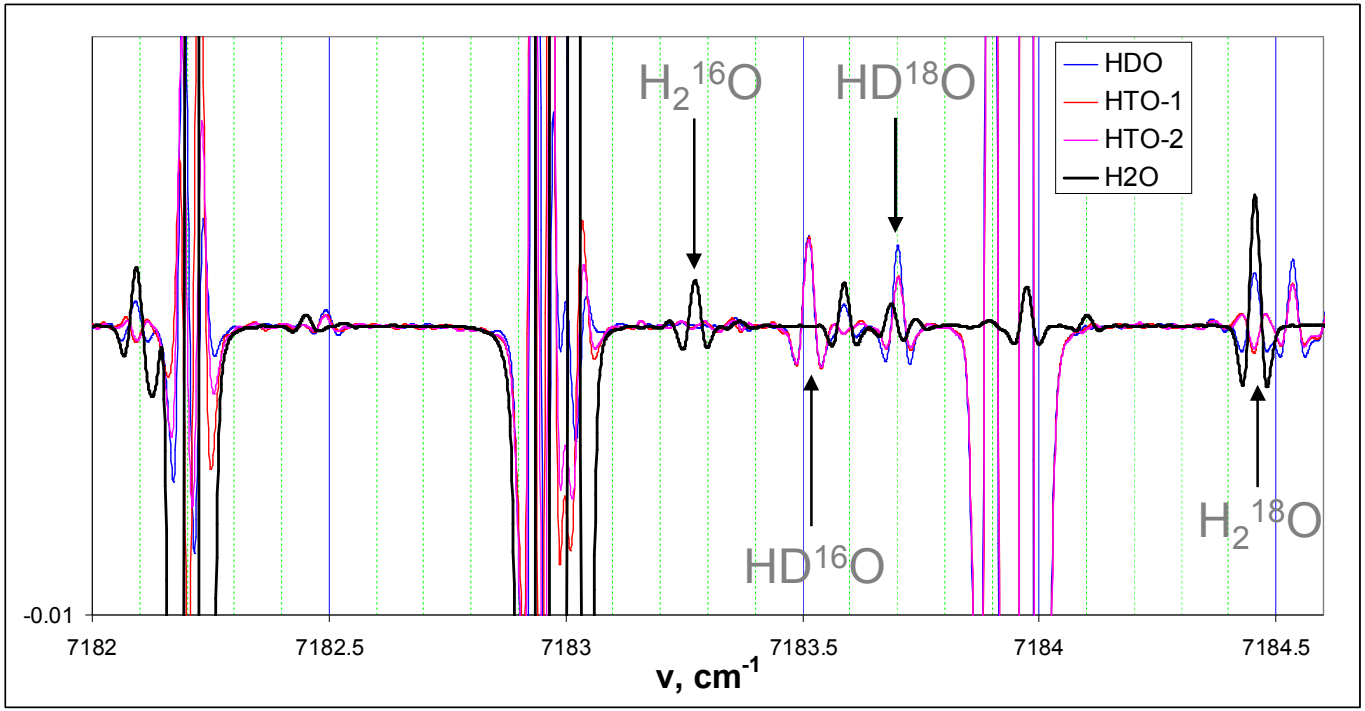
Spectra of 3 water samples were recorded using TDLS in spectral range 7166 – 7192 cm^{-1} (L = 2 m). Sample H2O – natural water; Sample HDO – 50% of heavy water and 50 % of natural water; Sample HTO – 50% of heavy water from reactor and 50 % of natural water.



TDLS spectra of H2O (black) and HDO (red) samples

Spectral lines identification

Spectra of 3 water samples were recorded using TDLS in spectral range 7166 – 7192 cm^{-1} (L = 2 m). Sample #1 – natural water; Sample #2 – 50% of heavy water and 50 % of natural water; Sample #3 – 50% of heavy water from reactor and 50 % of natural water.

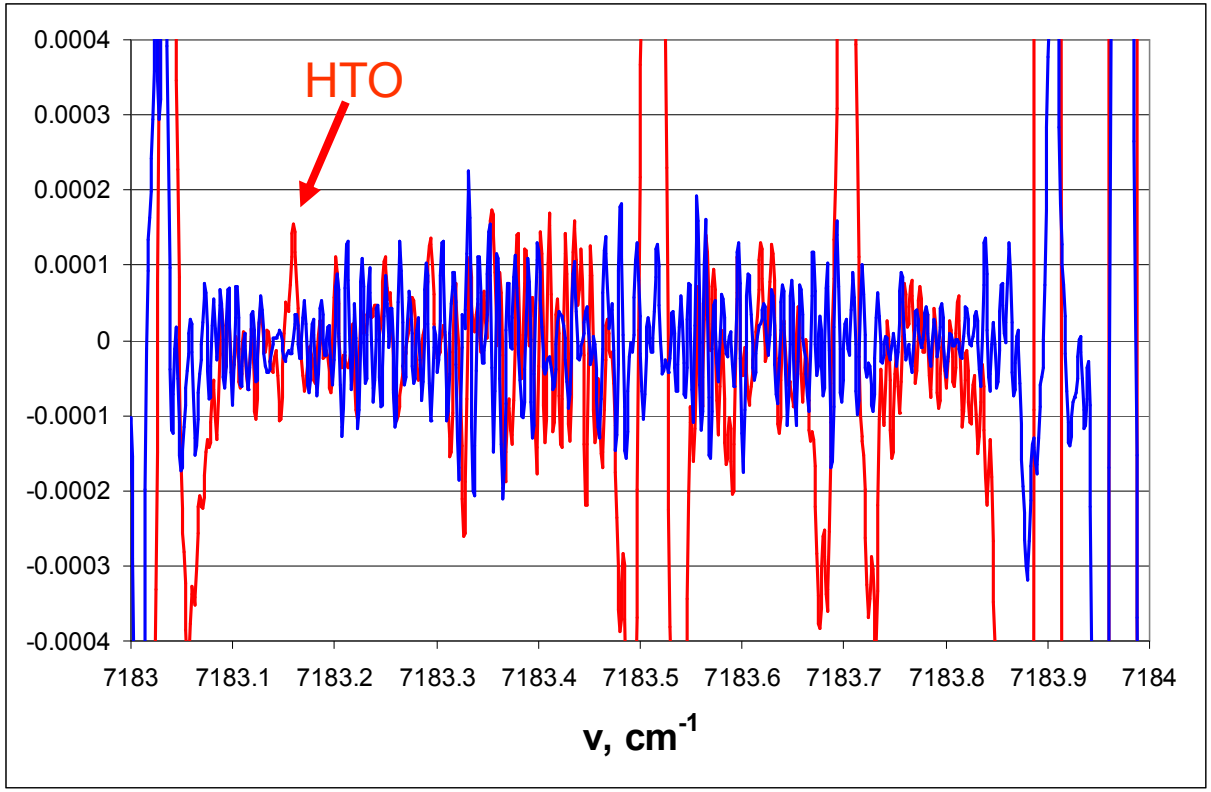


TDLS spectra of all samples #1 (black) and #2 (red)

Due to HITRAN, 38 lines here belongs to $HD^{16}O$. In present spectra 51 $HD^{16}O$ and 14 $HD^{18}O$ new lines were observed and measured.

TDLS spectra

Spectra of 3 water samples were recorded using TDLS in spectral range 7166 – 7192 cm^{-1} (L = 2 m). Sample #1 – natural water; Sample #2 – 50% of heavy water and 50 % of natural water; Sample #3 – 50% of heavy water from reactor and 50 % of natural water.

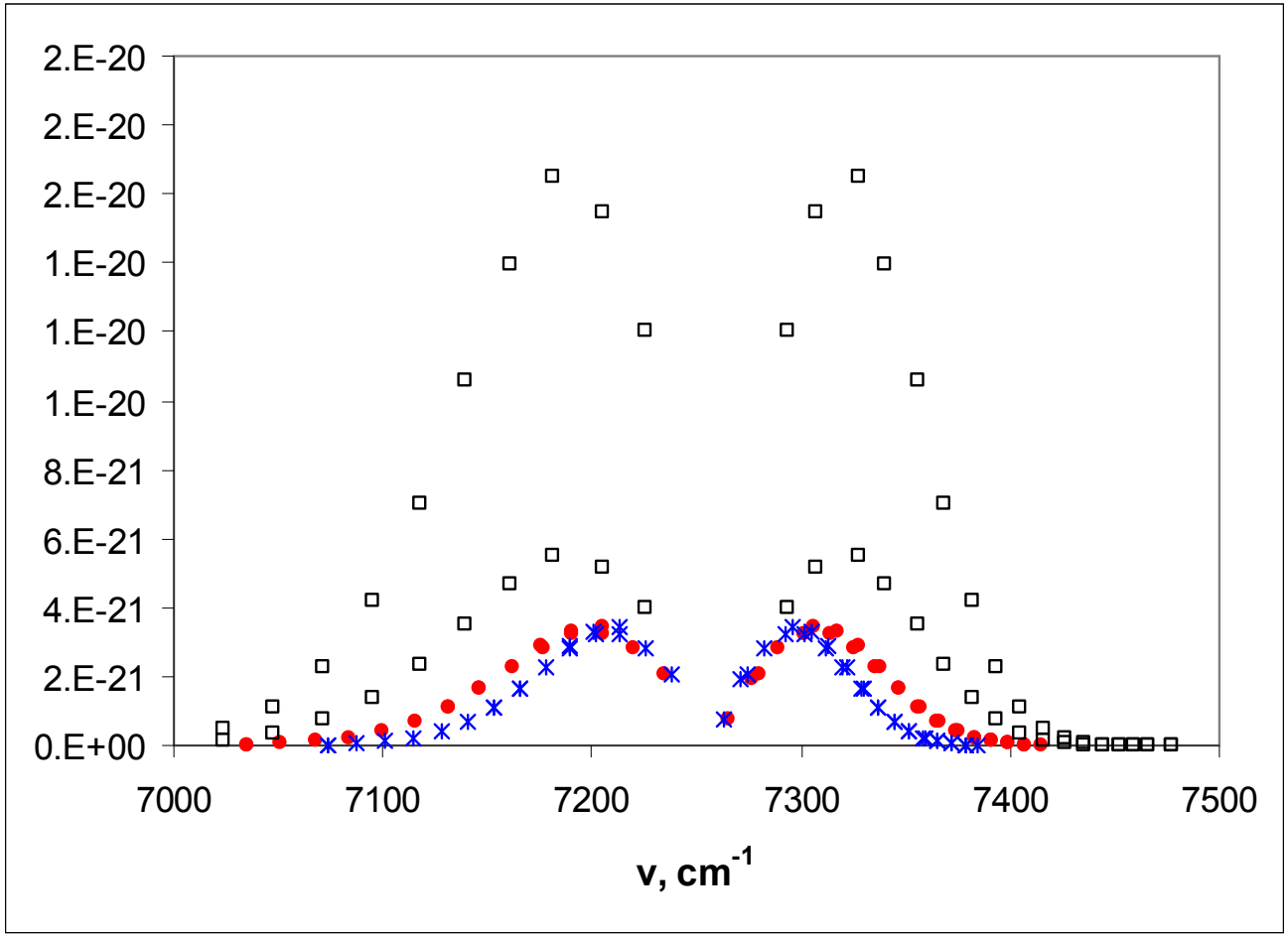


TDLS spectra of Samples #3 (red) and interference (blue)

In present spectra 12 HTO lines were observed and measured. Estimated T:D value was found to be of the order of 10^{-4}.

HTO calibration

Direct calibration of HTO is impossible. Hence, theoretical modeling is necessary.



Lines having largest integral intensity in J manifold of H_2O (black), HDO (red), HTO (blue).

HTO sensitivity estimation

L, m	39	Present cell
P, Torr	5	Low preasure
Absorbance	73	Calculated using HITRAN
NEA	1.00E-07	Measured NEA in our systems
NEP, Torr	1.37E-09	
NEN, 1/cm3	4.85E+07	
t, year	12	Half life time of tritium
t, days	4380	
t, sec	3.78E+08	
NEDecays, Bq/m3	1.28E+05	
Brasil, Bq/m3	2.20E+05	From Alvarez, Daniela (Brasil): "discharges numbers measured in the stack of one of our nuclear plants for tritium is 220000 Bq/m3"
NEDecays, μCi/m3	3.46	
Brasil, μCi/m3	6	

Noise equivalent HTO detection for present instrument is 3.5 μCi/m³. It is 10 times better than in mid IR [5] and is close to technical requirements.