

The use of quantum cascade lasers (QCL) is of great interest for both the spectroscopic investigation of molecular species and the in situ detection of trace gases in the atmosphere. The QCL lasers emit in the mid-infrared region with a high output power (of a few tens of mW), which enables to reach the strong fundamental rovibrational transitions of atmospheric gases. This laser technology has already been used for the field measurement of trace gases and detection limits as low as 2 parts in 10⁹ (ppb) were achieved, for instance, for the in situ detection of CH₄ and N₂O from the ER-2 stratospheric aircraft [1].

We have used a DFB quantum cascade laser (QCL) purchased from Alpes Lasers Inc. (Switzerland) emitting between 1480 and 1490 cm⁻¹ to carry out the spectroscopic study of the ν₂ band of H₂O and its isotopologues. The line strengths of some HDO transitions were revisited, which are suitable for the in situ probing of the middle atmosphere by absorption spectroscopy. Our laboratory spectroscopic measurements are compared with previous experimental determinations by Fourier-transform spectrometry as well as with calculations and available atmospheric molecular databases.

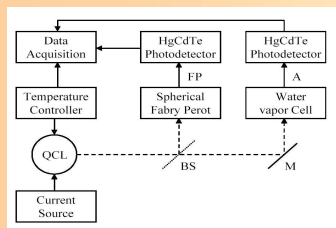
Our spectroscopic data were used to retrieve the concentration from atmospheric HDO spectra; first results obtained at ground levels are reported. Following this laboratory study, we intend to implement the QCL laser onboard the SDLA balloonborne diode laser spectrometer [2] to achieve in situ measurements of HDO in the upper troposphere (UT) and the lower stratosphere (LS) at high resolutions. The vertical concentration profiles of HDO could be of high interest to investigate convective processes coupling the UT and the LS in tropical regions as the heavy isotope features a preferential condensation phase [3].

[1] C.R. Webster et al. *Quantum-Cascade Laser Measurements of Stratospheric Methane and Nitrous Oxide*, Applied Optics, Volume 40, Issue 3, 321-326 (2001)

[2] Durry, G. and G. Megie, « Atmospheric CH₄ and H₂O monitoring with near-infrared InGaAs laser diodes by the SDLA, a balloonborne spectrometer for tropospheric and stratospheric in situ measurements », Applied Optics, 38, 7342-7354, (1999).

[3] Moyer, E. J., F. W. Irion, Y. L. Yung, and M. R. Gunson, *ATMOS stratospheric deuterated water and implications for troposphere-stratosphere transport*, GRL, 23, 2385 (1996).

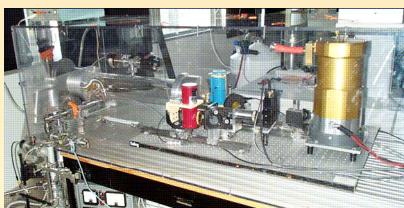
Presentation of the spectrometer



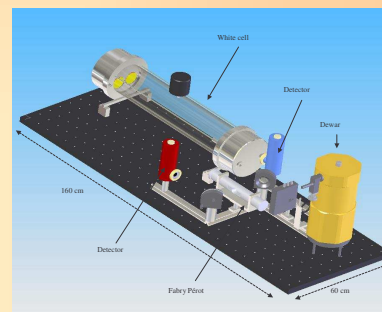
Scheme of the experimental set-up. QCL stands for quantum cascade laser, BS stands for beamsplitter and M stands for mirror.

The light source is a continuous-wave distributed feedback quantum cascade laser (cw-DFB QCL) from Alpes Lasers inc., Switzerland. It emits near 6.7 μm. The frequency region is from 1483 cm⁻¹ to 1487 cm⁻¹, and the spectra are recorded with a temperature ramp from 80K to 125K. The laser needs nitrogen liquid cooling, which is provided by a house-built cryostat (see photo below).

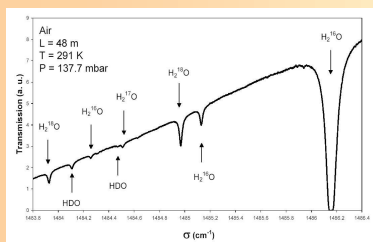
The laser beam is separated in two parts : the reflected beam is coupled with a spherical Fabry-Pérot, the second beam passes through the cell. The measurements are realized with ambient air or with enriched water for spectroscopic parameters determination. The complete apparatus is placed into a closed box filled with dry nitrogen in order to avoid corruptions by ambient water vapor.



Photograph of the experimental set-up.



3D-view of the experimental set-up. The dewar adapted to the QCL device was developed in our lab. The dewar is filled with liquid nitrogen every 8 hours. During this period the laser is fully operational which is well adapted for field measurements.



Experimental spectrum of air from 1483.8 cm⁻¹ to 1486.4 cm⁻¹. Experimental conditions are given on the figure. The measurement time is approx. 30 seconds.

Determination of isotopologues parameters

Line number	Isotopologue	Band	Transition	σ_i (cm ²)	S (cm ⁻¹ /(molecule.cm ²)) HITRAN 2004	S (cm ⁻¹ /(molecule.cm ²)) JOLY et al	Difference (%)
1	H ₂ ¹⁶ O	ν ₂	6 ₁₆ ← 6 ₂₅	1483.92607	8.391 10 ⁻²³	9.054 10 ⁻²³	7
2	HDO	ν ₂	6 ₁₆ ← 5 ₁₅	1484.10644	2.324 10 ⁻²³	2.528 10 ⁻²³	8
3	H ₂ ¹⁶ O	ν ₂	10 ₁₆ ← 11 ₁₇	1484.25726	1.779 10 ⁻²³	-	-
4	HDO	ν ₂	4 ₃₁ ← 3 ₃₀	1484.47016	3.534 10 ⁻²⁴	3.766 10 ⁻²⁴	6
5	H ₂ ¹⁶ O	ν ₂	2 ₁₁ ← 3 ₂₂	1484.51094	1.973 10 ⁻²³	-	-
6	H ₂ ¹⁸ O	ν ₂	4 ₁₈ ← 5 ₁₅	1484.97157	1.021 10 ⁻²²	1.083 10 ⁻²²	6
7	H ₂ ¹⁶ O	2ν ₂ -ν ₂	3 ₂₁ ← 3 ₃₀	1485.13360	6.253 10 ⁻²³	6.141 10 ⁻²³	-2
8	H ₂ ¹⁸ O	ν ₂	9 ₁₈ ← 9 ₂₇	1486.15840	4.397 10 ⁻²¹	4.228 10 ⁻²¹	-4

List of the main lines with increasing wavenumber that can be reached with our quantum cascade laser. These lines are noted on the figure.

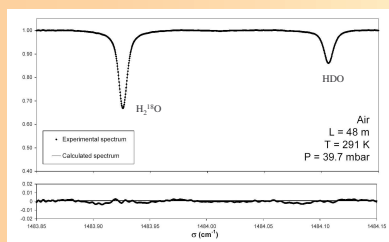
Molecular parameters of selected transitions have to be very well known. We measured them with the method previously described and compared them with experimental or calculated results of other studies.

The figure on the right shows the spectrum recorded with a frequency scanning of the laser provided by a temperature ramp. Eight strong transitions can be measured : two of H₂¹⁸O, two of H₂¹⁶O and four of HDO. A H₂¹⁷O is also present but can not be easily measured because of a weaker HDO line.

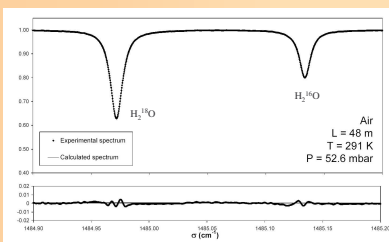
Our measurements agree well with other results.

Water vapor isotopologues concentration measurements

Laboratory measurements of air samples



Experimental spectrum of air from 1483.85 cm⁻¹ to 1484.15 cm⁻¹. This current excursion enables to cover 2 water vapor isotopologues : H₂¹⁸O and HDO (Lines #1 and #2) within approx. 1 s. Experimental conditions are given on the figure. The experimental profile and a calculated Voigt profile are given on the figure with the residual.



Experimental spectrum of air from 1484.90 cm⁻¹ to 1485.20 cm⁻¹. This current excursion enables to cover 2 water vapor isotopologues : H₂¹⁸O and H₂¹⁶O (Lines #6 and #7) within approx. 1 s. Experimental conditions are given on the figure. The experimental profile and a calculated Voigt profile are given on the figure with the residual.

Lines #1, #2, #6 and #7 are used for the retrieval of the isotopologues concentrations. The concentration derived from the fitting procedure are reported in the table and compared with the calculations based on the saturated vapor pressure in air at the temperature measurements and the partial water vapor pressure obtained from a hygrometer. We can see that the retrieved concentration for isotope H₂¹⁸O is the same for two different lines. The concentration obtained from the fitting procedure and those of the hygrometer are in quite good agreement for H₂¹⁸O and H₂¹⁶O. The HDO value is quite different.

Line number	Isotopologue	Mean concentration	Uncertainty	Hygrometer concentration	Uncertainty
1	H ₂ ¹⁸ O	2.09 10 ⁻⁵	0.26 10 ⁻⁵	1.97 10 ⁻⁵	0.22 10 ⁻⁵
2	HDO	4.93 10 ⁻⁶	0.45 10 ⁻⁶	3.06 10 ⁻⁶	0.34 10 ⁻⁶
6	H ₂ ¹⁶ O	2.11 10 ⁻⁵	0.26 10 ⁻⁵	1.97 10 ⁻⁵	0.22 10 ⁻⁵
7	H ₂ ¹⁶ O	1.06 10 ⁻²	0.09 10 ⁻²	0.98 10 ⁻²	0.11 10 ⁻²

Measured concentrations and comparison with the results obtained with the hygrometer.

For each sample, the measured isotopic ratio in ppm are given by $R^{18} = [H_2^{18}O] / [H_2^{16}O] \times 10^6$ and $R^D = [HDO] / 2[H_2^{16}O] \times 10^6$. The mean values are reported in the table and compared to the standard isotopic ratios (R_{STD}) from Standard Mean Ocean Water. δ is defined in ‰ for the two isotopologues by: $\delta^X = 1000 \times \frac{R_{exp} - R_{STD}}{R_{STD}}$ where X = 18 or D from the experiment.

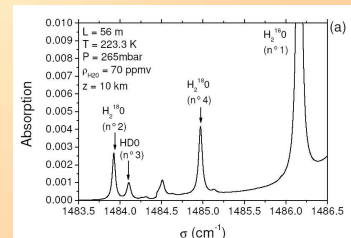
The δ mean value of the two isotopologues are also reported in the table. Eight independent measurements yielded mean values of δ_{18} of 1‰ for the first retrieved line and 9‰ for the second line. The estimated standard deviation was 60%. This value shows the very good agreement between the measurements and the standard isotopic ratios. The same eight independent measurements yields values of δD varying from +420 to +560‰ with a mean value of 517‰ and a estimated standard deviation of 55%. According to the global network for isotopes in precipitation (GNIP) database, δD varies from 0 to -300‰ with geographic region and times. Our values does not seem reasonable. However the White cell used for static measurements was used previously for the intensity measurements of HDO in the laboratory. Our cell was probably polluted by the outgassing of HDO trapped in the used optical cell during the previous laboratory experiment.

Line number	Isotopologue	Measured isotopic ratio (ppm)	Standard isotopic ratio (ppm)	Delta (‰)
1	H ₂ ¹⁸ O	2006	2005.2	1
2	HDO	236.3	155.8	517
6	H ₂ ¹⁶ O	2023	2005.2	9

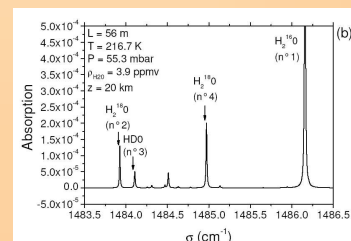
Measured isotopic ratios and delta values.

Purpose

Water is the most important greenhouse gas. The stratosphere is strongly dehydrated but an increase of around 1% per year has been noticed. Sources and sinks in middle stratosphere are yet poorly understood. The measurement of heaviest isotopes of water (like HDO) can give information about the injection of water in stratosphere as they present a preferential condensation phase, thus leading to an enrichment or a depletion of air parcel during its convective elevation. It would be of high interest to mount a spectrometer capable to detect this isotopes on balloonborne spectrometer SDLA (already used for in situ monitoring of H₂O and CH₄ in the UT-LS [2]). This requires a good detection limit (10⁻³cm⁻¹) which is feasible with the developed differential detection technique.



Synthetic spectrum of water isotopes in tropospheric conditions (10km)



Synthetic spectrum of water isotopes in stratospheric conditions (20km)